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RESULTS OF A GREENHOUSE STUDY INVESTIGATING THE PHYTOEXTRACTION OF LEAD FROM CONTAMINATED SOILS OBTAINED FROM THE SUNFLOWER ARMY AMMUNITION PLANT

Desoto, Kansas

Prepared for
U.S. ARMY ENVIRONMENTAL CENTER
Aberdeen Proving Ground, Maryland 21010-5401

Prepared by
Tennessee Valley Authority
Environmental Research Center
Muscle Shoals, Alabama 35662-1010

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Prepared for
U.S. Army Environmental Center
Pollution Prevention and Environmental Technology Division
Aberdeen Proving Ground, Maryland 21010-5401
POC: Ms. Darlene F. Bader

Prepared by
A. D. Behel, R. A. Almond,
D. A. Kelly, P. A. Pier, and W. J. Rogers
of the
Tennessee Valley Authority
Muscle Shoals, Alabama 35662-1010

AND

Darlene F. Bader
of the
U.S. Army Environmental Center
Pollution Prevention and Environmental Technology Division
Aberdeen Proving Ground, Maryland 21010-5401

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This report describes the results of greenhouse studies conducted to determine if phytoextraction methods could be enhanced by increasing ionic lead's solubility in water. Soil acidifiers and chelating agents were used to increase lead's solubility in water. The study was conducted using lead contaminated soil from the Sunflower Army Ammunition Plant near Desoto, Kansas. These soils were shipped to the Tennessee Valley Authority's Environmental Research Facility in Muscle Shoals, Alabama, where the study was conducted. The report concludes that phytoextraction methods may be enhanced by these techniques and that the risk of leaching lead out of the soil's root zone is minimal.

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EXECUTIVE SUMMARY

The U.S. Army Environmental Center (USAEC) funded this project as part of the Department of Defense's (DoD) program to evaluate remediation technologies for removing heavy metals from contaminated soils. Of the heavy metals, the DoD is currently emphasizing lead (Pb) removal due to the inherent toxicity of lead and the quantity discharged. A number of DoD installations have soils which will require remediation for heavy-metal contamination. The contamination consists of both particulate and ionic metals. The metallic particulate (bullet fragments, etc.) were often deposited as the result of firing range use. The ionic metals were commonly deposited when metal-bearing propellants, ammunitions, and powders were burned at explosive disposal sites. The project goal was to determine how to increase the effectiveness of phytoextraction techniques for removing ionic lead from contaminated soils. The project was conducted in support of an Environmental Security Technology Certification Program (ESTCP) proposal to conduct a field demonstration of phytoextraction techniques. Based on the results of this project, a two year field demonstration was funded in fiscal 1998 and is currently being conducted at the Twin Cities Army Ammunitions Plant (TCAAP).

Phytoextraction is an *in situ* remediation method in which plants are used to remove ionic metals, particularly lead, from contaminated soils. During the phytoextraction process, water-soluble metals are taken up by plant species selected for their ability to take up large quantities of lead. The metals are stored in the plant aerial shoot tissues which are harvested and are either smelted for potential metal recycling/recovery or are disposed of as a hazardous waste. Phytoextraction is generally considered a subcategory of phytoremediation, which is a broad term for a variety of remediation methods which use plants to remediate contaminated soils, surface waters, and groundwaters.

The primary objective of this project was to determine whether enhancing the solubility of soil-borne lead would be a practical and affordable method of improving phytoextraction techniques for remediating lead-contaminated soils. The solubility of lead was to be increased by adjusting the soil pH and adding chelating agents to the soil. Specific project objectives were to:

- Select the chelate, chelate concentration, and soil pH level that optimized lead solubilization in soil.

- Determine the optimum method for applying the soil amendments (soil acidifiers and chelates).

- Monitor chelate movement and degradation in soil over time.

- Select the treatment combination (plant species and soil amendment concentrations, etc.) that optimized lead uptake and promoted translocation of lead to plant shoots.

- Determine if lead leaches out of the root zone when soil amendments are applied under simulated field conditions and, if so, to what extent.

This project was executed under a partnering agreement between the USAEC and the Tennessee Valley Authority (TVA). The USAEC was the lead agency. The U.S. Army Corps of Engineers (USACE) Kansas City District and the U.S. Army's Industrial Operations Command (IOC) provided contaminated soil from the Sunflower Army Ammunition Plant (SFAAP) at Desoto, Kansas. TVA conducted the study and provided technical expertise in plant lead uptake, application of soil amendments, and analysis of soil and plant samples.

Based on the project results, TVA concluded that the optimum treatment parameters were:

- Use of corn (*Zea mays Mays* L.) as a warm season crop.
- Use of white mustard (*Brassica hirta* L.) as a cool season crop.
- Use of the potassium salt of ethylene-dinitrilo-tetraacetic acid (EDTA) as the chelate at a 1.0 molar ratio of chelate to soil-borne lead.
- The EDTA should be applied with only enough water to bring the top two feet of soil to field capacity.
- Acidification of soil pH to 5.5 using acetic acid in conjunction with EDTA when corn is the phytoextraction crop.
- No soil acidification with use of EDTA when white mustard is the phytoextraction crop.

- If needed to provide supplemental phosphorus, a 1 percent foliar phosphate spray may be used for corn.
- A foliar phosphate application should not be made when growing white mustard.

The project results indicate that:

- Lead levels in the treated soils were reduced by a maximum of 8% depending upon soil type, fertilization levels, and the crop grown.
- Average lead concentrations in corn and white mustard were 0.85% and 1.5% by weight, respectively.
- Foliar application of phosphates to corn did not significantly affect the corn crop's ability to take up lead.
- The optimum time to harvest corn (after soil acidification and EDTA application) was after plants had senesced to the point of dryness, but still contained sufficient moisture to prevent excessive leaf shatter.
- When using white mustard, the optimum time to apply EDTA is at the onset of bolting and flowering.
- With white mustard, maximum lead uptake occurred within 48 hours after EDTA application. Harvesting at this point will minimize the potential for leaf shatter and wind dispersion.
- As long as the moisture content of the soil was held to field capacity or below, solubilized lead and water-soluble EDTA generally remained within the plant root zone.

Overall, the project results were encouraging. Based on these results, the phytoextraction methods examined are likely to enhance lead removal with minimal risk of lead leaching out of the root zone.

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ABBREVIATIONS

AA	Atomic Absorption
AAP	Army Ammunition Plant
AL	Alabama
Al	Aluminum
Ca	Calcium
Cd	Cadmium
CDTA	Cyclohexane-1,2-Diaminetetraacetic Acid
CEC	Cation Exchange Capacity
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
cmole	centimole (100^{th} of a mole)
Cr	Chromium
Cu	Copper
DoD	Department of Defense
DOT	Department of Transportation
ESTCP	Environmental Security Technology Certification Program
EDTA	Ethylene-dinitrilo-tetraacetic acid
EGTA	Ethylene bis(oxyethylenetrinitrlo)tetraacetic acid
EPA	Environmental Protection Agency
ERC	Environmental Research Center
Fe	Iron
FIA	Flow Injection Analyzer
Hg	Mercury
HPLC	High Performance Liquid Chromatography
ICP	Inductively Coupled Plasma
IOC	Industrial Operations Command
K	Potassium
kg	Kilograms
$LSD_{0.05}$	Least significant difference at the 5% probability level.
MDL	Method Detection Limit
meq	millequivalent
Mg	Magnesium
mg	Milligrams
ml	Milliliter
Mn	Manganese
Mo	Molybdenum
NC	Nitrocellulose
NG	Nitroglycerin
Ni	Nickel
NQ	Nitroguanidine
NS	Not significant
P	Phosphorus
Pb	Lead

ABBREVIATIONS (Continued)

PEL	Permissible Exposure Limit
ppm	Parts Per Million
QA	Quality Assurance
QC	Quality Control
Se	Selenium
SEM	Scanning Electron Microscope
SFAAP	Sunflower Army Ammunition Plant
TCAAP	Twin Cities Army Ammunition Plant
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TVA	Tennessee Valley Authority
µg	Microgram
USACE	United States Army Corps of Engineers
USAEC	United States Army Environmental Center
Zn	Zinc

SECTION 1.0
INTRODUCTION

1.1 Background

The U.S. Army Environmental Center (USAEC) funded this project as part of a Department of Defense (DoD) program to evaluate remediation technologies. The project goal was to determine how to increase the effectiveness of phytoextraction techniques for extracting ionic lead (Pb) from contaminated soils. The project was conducted in support of an Environmental Security Technology Certification Program (ESTCP) proposal to conduct a field demonstration of phytoextraction techniques.

Phytoextraction is an *in situ* remediation method in which plants are used to remove ionic metals, in this case lead, from contaminated soils. During the phytoextraction process, metals solubilized by soil amendments are taken up by plant species selected for their ability to take up large quantities of lead. The metals are stored in the plant aerial shoot tissues, which are harvested and are either smelted for potential metal recycling/recovery or are disposed of as a hazardous waste. Phytoextraction is generally considered a subcatergory of phytoremediation, which is a broad term for a variety of remediation methods which use plants to remediate contaminated soils, surface waters, and groundwaters.

A number of DoD installations have heavy metal-contaminated soils requiring remediation. Particulate heavy metals (bullet fragments, etc.) were deposited during the expenditure of munitions on firing ranges. In addition, ionic metals were commonly deposited when metal-bearing propellants, ammunitions, and powders were burned at explosive disposal sites. CERCLA has identified heavy metals, lead in particular, as a priority concern. Because of the inherent toxicity of lead and the quantity discharged, the DoD is currently emphasizing lead removal. Hence, a cost-effective process for removing lead from contaminated soils is needed.

One constraint to the use of phytoextraction techniques is the low solubility of lead in soil; hence, it is difficult for plants to absorb lead through their root systems. Conceptually, increasing lead solubility in the soil should enhance plant uptake and translocation of lead to shoot tissues.

The solubility of soil-borne lead can be increased by lowering the soil pH and by adding chelates to the soil. The technique is based on the behavior of chelates in soil. Simplistically, metal chelation may be viewed as a multiple bonding of metal ions to the coordinating groups (or ligands) of organic compounds to form a stable charge structure. The stability of the metal chelate complex protects the metal ion and minimizes reaction with soil. The metal ion's solubility is increased by the ligands with which it becomes coordinated and the solubilized metal is more readily removed from soil.

An additional challenge to phytoextraction is the tendency of lead to accumulate within most plant root structures, rather than moving to the aerial shoots. Prior research [Ref.1], indicated that lead translocation to the shoots of selected plant species was enhanced when chelates were present in soil, resulting in the accumulation of up to 2% lead in the aerial portion. Hence, it may be possible to improve phytoextraction efficiency. The goal of this project was to determine the impact of chelate use, soil pH adjustment, and selected plant species on the efficiency of current phytoextraction techniques. Determining the impact of these factors was necessary in order to assure the success of the proposed ESTCP field demonstration.

This project was executed under a partnering agreement between the:

- U.S. Army Environmental Center (USAEC)
- Tennessee Valley Authority (TVA)

The USAEC was the lead agency. The U.S. Army Corps of Engineers (USACE) Kansas City District, and the U.S. Army's Industrial Operations Command (IOC) provided contaminated soil from the Sunflower Army Ammunition Plant (SFAAP) at Desoto, Kansas. TVA conducted the study and provided technical expertise in plant lead uptake, soil amendment application, and metals analysis for soil and plant samples. This document serves as the project's Final Results Report.

1.2 Project Objectives

This project's primary objective was to determine whether enhancing the solubility of lead in soil would be a practical and affordable method for phytoextracting lead from contaminated soils. Specific objectives were to:

- Select the chelate, chelate concentration, and soil pH level to optimize lead solubilization.
- Determine the optimum method for applying the soil amendments (soil acidifier and chelate).
- Monitor the chelate movement and degradation in soil over time.
- Select the treatment combination (plant species, soil amendment concentration, and foliar phosphate fertilization) that optimizes lead uptake and promotes translocation to the shoot.
- Determine the extent that lead leaches out of the root zone when soil amendments are applied.

1.3 Approach

The project was executed in five phases, these being:

- Test Plan Development (Phase 1). During this phase, the project was planned and developed.
- Site Screening, Soil Collection, and Metal Analysis (Phase 2). During this phase, contaminated soils at various sites were considered for use, selected, collected, and analyzed for pH and heavy metals content.

- Preliminary Laboratory Studies (Phase 3). This phase contained two studies: one for chelate screening (the Chelate Screening Study) and another addressing chelate application (the Chelate Applications Study). The purpose of these studies was to assess the variables affecting lead solubilization (i.e., chelate type, concentration, soil pH, and soil application method) and to monitor soil amendment movement and fate.

- Greenhouse Studies (Phase 4). This phase originally contained three greenhouse studies: one pot study for screening plant species (the Plant Screening Study); a second pot study addressing the foliar application of phosphate nutrients (the Foliar Application Study); and a third study in which the most effective plant species, soil amendment treatments, and fertilizer levels from two previous greenhouse studies were used in larger volumes of soil to assess leaching of lead and EDTA (the Soil Leaching Study). The Soil Leaching Study also included an after-harvest replanting to determine the effect of lead and residual chelate on seed germination and plant growth, leaching of lead by residual chelate, and lead removal by subsequent planting.

  During the project, the scope of Phase 4 was increased to include three additional studies: a Lysimeter Study to more accurately monitor EDTA and lead movement through soil; a Chelate Timing Study to determine if lead uptake could be increased by adding a chelate when white mustard's water use was at a maximum; and a Harvest Timing Study to determine the time required for white mustard to take up lead after EDTA has been added to the soil.

- Final Report Writing (Phase 5). During this phase, the final report was written.

The project started the fall of 1996 with test plan development (Phase 1), contaminated site screening (Phase 2), and the transport of selected soil to TVA's facilities (Phase 2). During Phase 2, lead-contaminated soil was collected from an explosives burning ground located at the SFAAP in Desoto, Kansas, and brought to TVA's facility in Muscle Shoals, Alabama, where the lead uptake project was performed.

When the soil arrived, a preliminary assessment was initiated (Phase 3) to determine which soil amendments should be used, how the amendments should be applied, and the fate of the

amendments in soil. Concurrent with the preliminary assessment, plants were grown for use in the Plant Screening Study (Phase 4). During Phase 4, the selected soil amendments were applied when the plants reached full vegetative biomass (i.e., to a stage just before grain production).

During the Plant Screening and Foliar Application Studies (Phase 4), soil amendments were applied to the potted plants to facilitate lead uptake. Within two to four days, the plants began to senesce (die) due to lead uptake. The plants were harvested after they died. The plant shoots and soil were then analyzed for lead concentration. The plant dry matter content was also determined.

After the Foliar Application Study, the Soil Leaching Study was initiated (Phase 4). During the Soil Leaching Study, columns containing approximately 17 kg of soil were planted with the best warm and cool season species from the previous study. When the first crop reached full vegetative biomass, the soil amendments were added. The soil was sampled both before soil amendment addition and after harvesting the first crop. These soils were analyzed for lead and other heavy metals. The plant shoots were analyzed for heavy metals content after harvest. Prior to adding soil amendments, an attempt to collect the leachate was made every two weeks. After the soil amendments were added, an attempt to collect leachate was made daily until plant harvest. However, poor percolation in these soils prevented leachate collection. The reasons for this are discussed in Section 5.3.3.

After the initial harvest, the containers were replanted with the second crop. However, the second crop either failed to germinate or died shortly after germination, except for the contral columns (with no soil amendments) from the first planting. These plants were grown to full vegetative biomass, soil amendments were applied, and the plants were harvested and analyzed for lead, heavy metals, and chelate content. The reasons for these crops failures are discussed in Section 5.3.3.

After the Soil Leaching Study, the Lysimeter Study was initiated (Phase 4). The procedures for Lysimeter Study were very similar to the Soil Leaching Study. The study scope consisted of:

- Treatment with the cool season crop

- One soil type (due to a lack of soil)
- No controls (due to a lack of soil)

Finally, the Chelate Application Timing and Harvest Timing Studies were initiated (Phase 4). The purpose of these studies was to optimize the lead uptake by the cool season crop.

During the project's final phase, Phase 5, the final report was written.

1.4 Schedule

A GANTT chart showing project-related activities is provided in Figure 1-1. As indicated in the section above, there were five phases to this study. The timelines for these phases were:

- Test Plan Development (Phase 1). Began on September 6, 1996, and was scheduled to end on December 8, 1996.

- Site Screening, Soil Collection, and Metals Analysis (Phase 2). Began on August 6, 1996, and was scheduled to end on December 9, 1996.

- Preliminary Laboratory Studies (Phase 3). Began on December 9, 1996, and was scheduled to end on March 8, 1997. Studies conducted within this phase had timelines as follows:
  - ⇒ Chelate Screening Study - December 9, 1996, to December 23, 1996
  - ⇒ Chelate Application Study - December 16, 1996, to March 8, 1997

- Greenhouse Studies (Phase 4). Began on November 29, 1996, and was scheduled to end on January 7, 1998. Studies to be conducted within this phase had timelines as follows:
  - ⇒ Plant Screening Study - November 29, 1996, to April 28, 1997
  - ⇒ Foliar Application Study - March 18, 1997, to August 5, 1997
  - ⇒ Soil Leaching Study - May 19, 1997, to May 8, 1998
  - ⇒ Lysimeter Study - October 19, 1997, to January 20, 1998

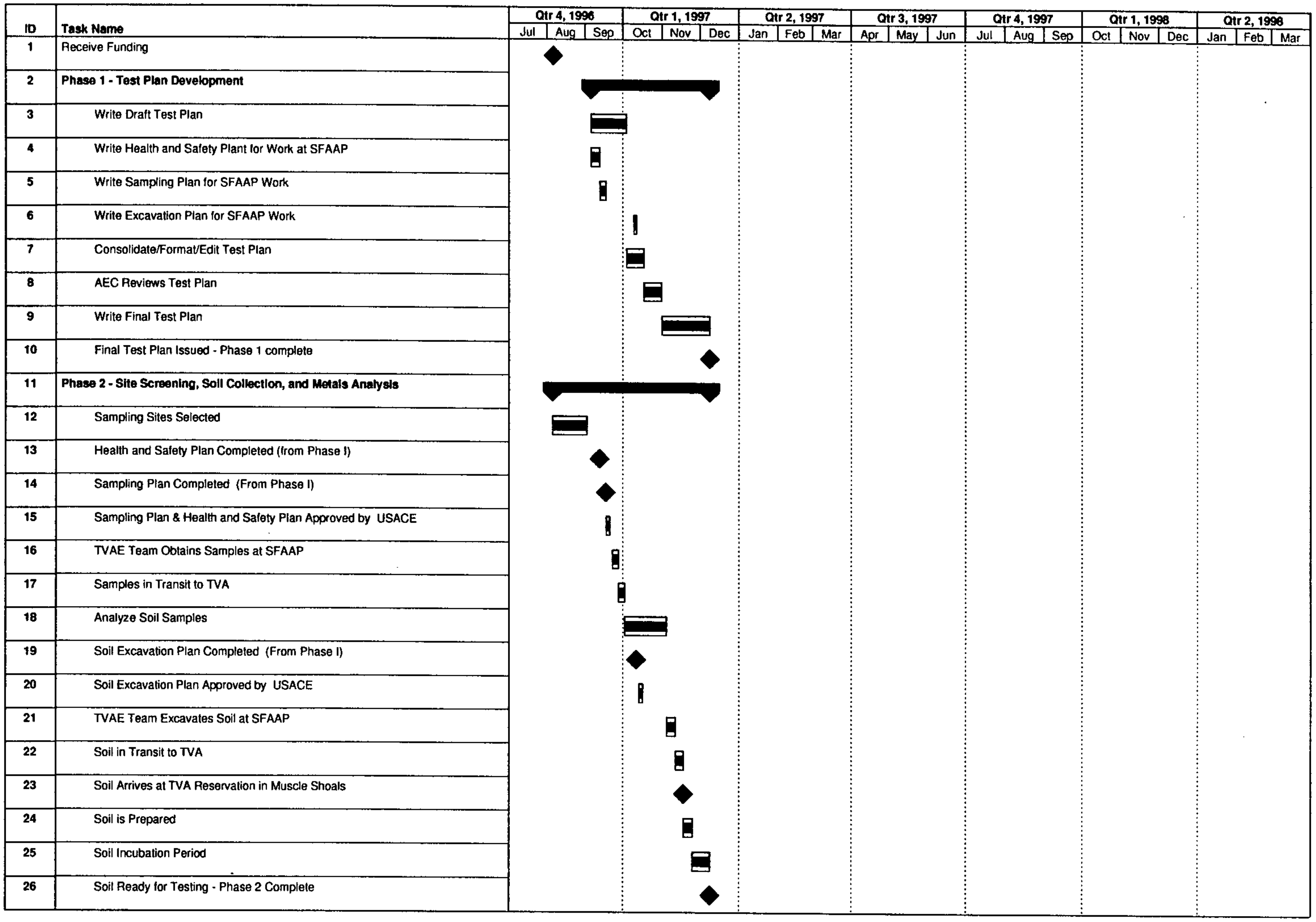


Figure 1-1

GANTT Chart for Lead Uptake Project

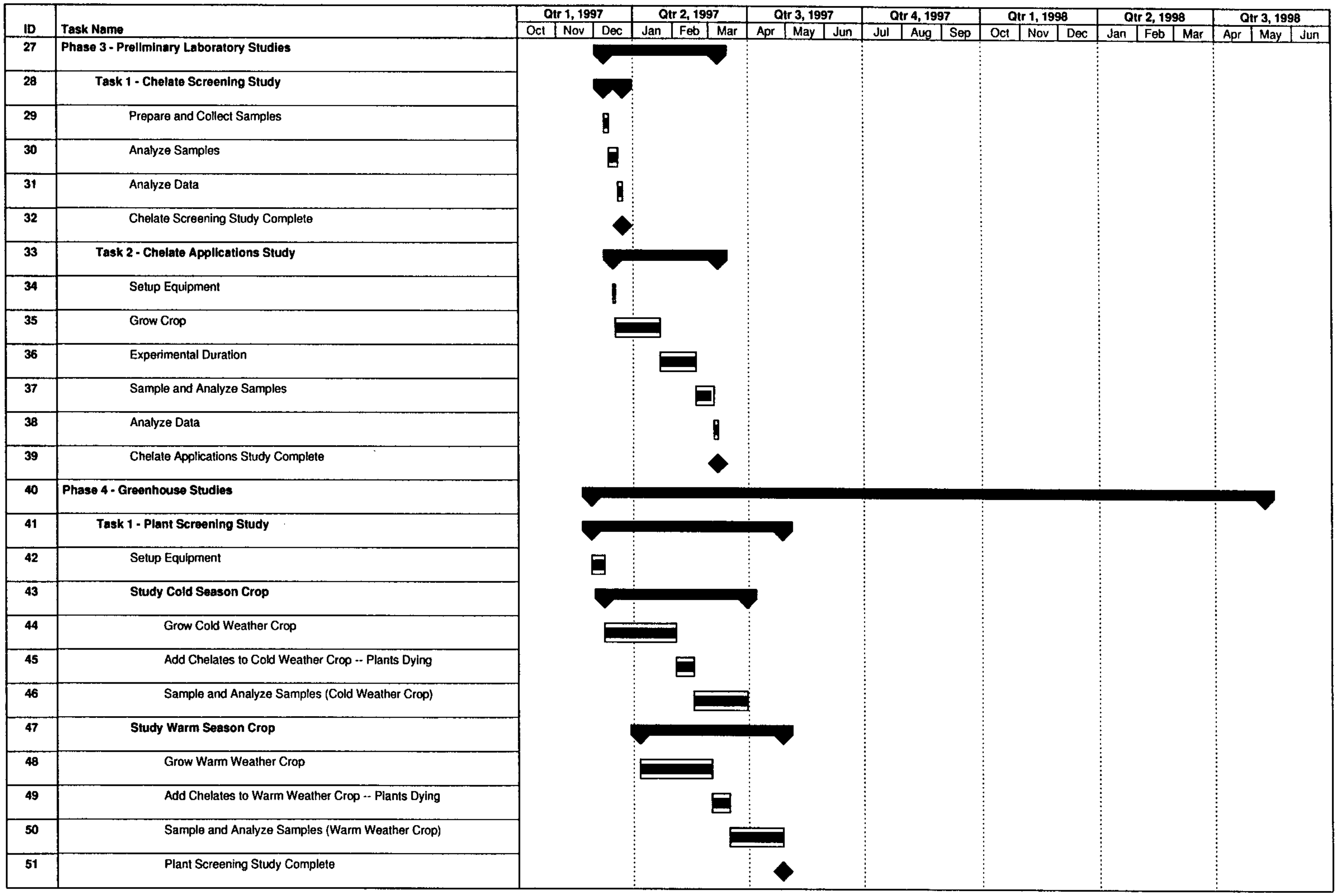
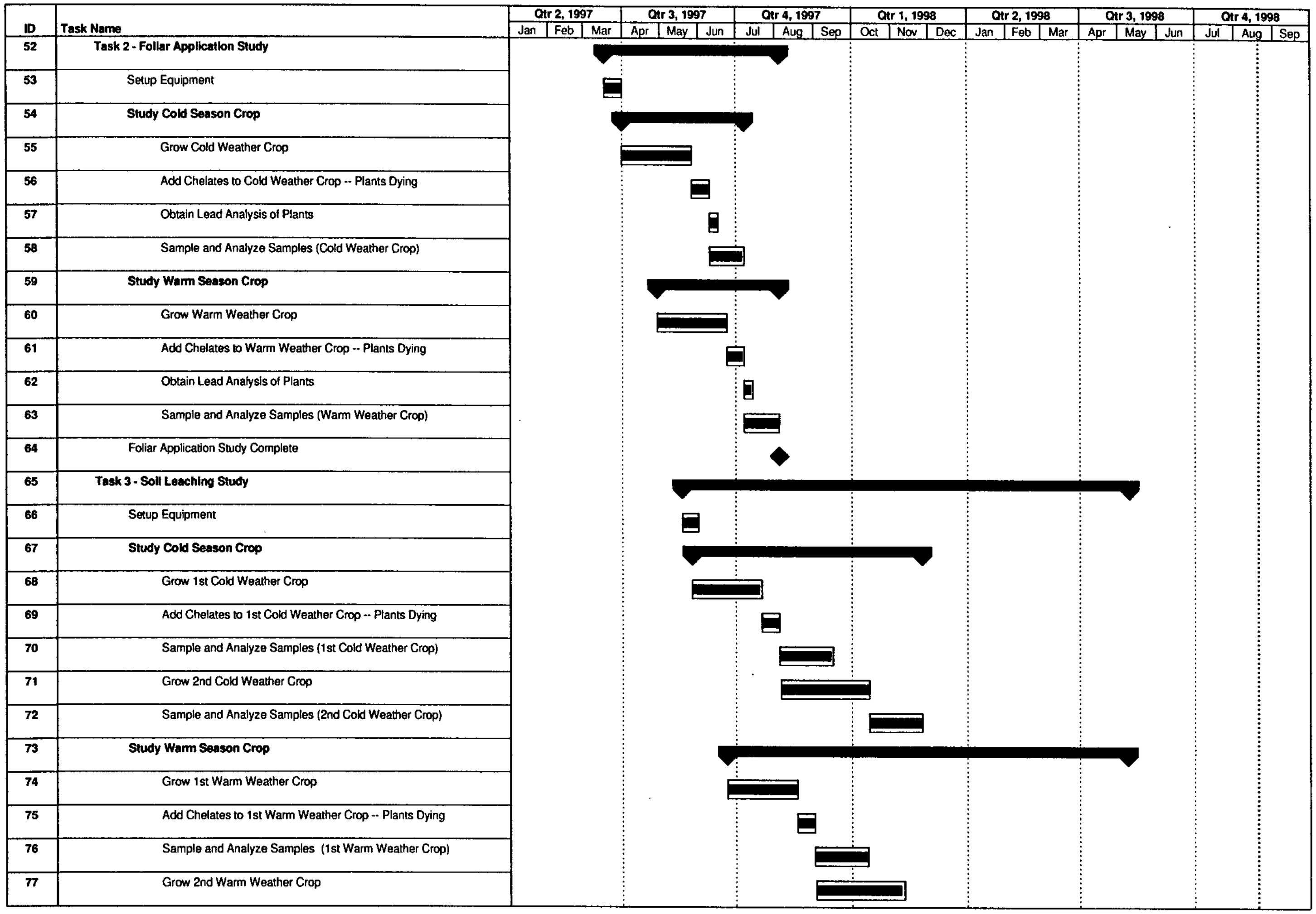


Figure 1-1 (Continued)

GANTT Chart for Lead Uptake Project



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GANTT Chart for Lead Uptake Project

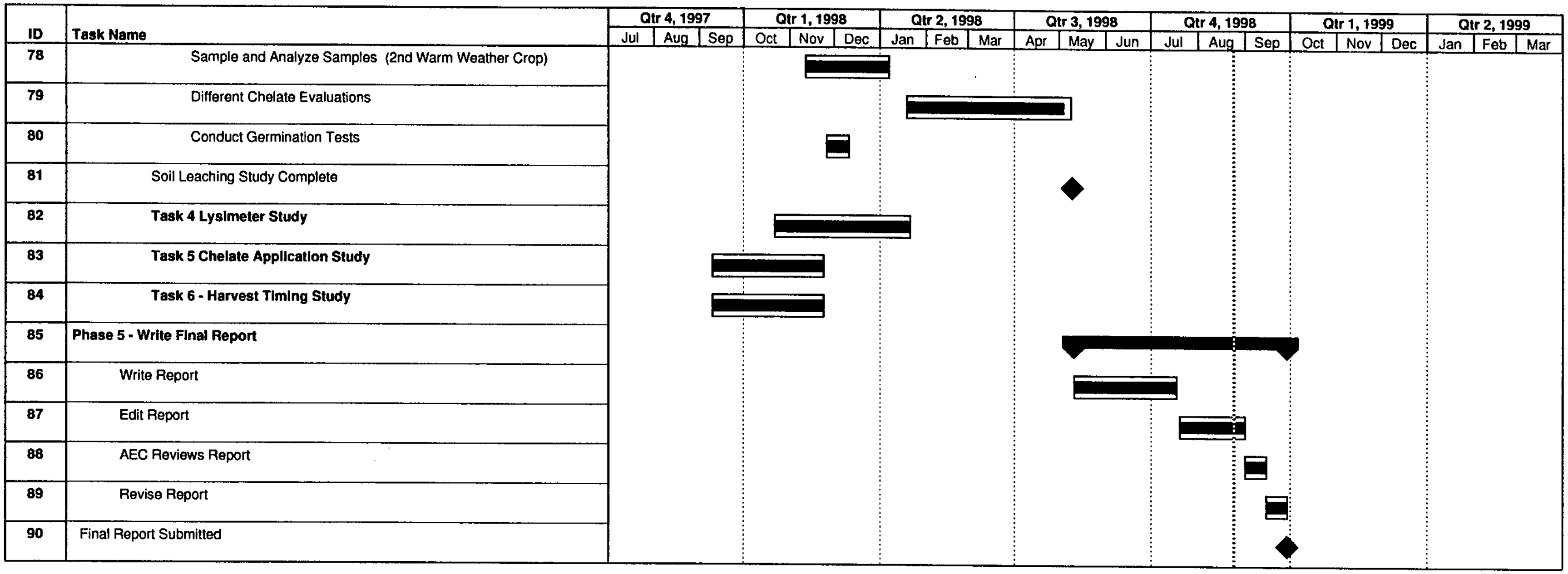


Figure 1-1 (Continued)

GANTT Chart for Lead Uptake Project

- ⇒ Chelate Application Timing Study - September 10,1997, to November 23, 1997
- ⇒ Harvest Timing Study - September 10,1997, to November 23, 1997

- Final Report Writing Phase (Phase 5). Began on April 7, 1998, and ended September 29, 1998.

SECTION 2.0

LOCATION AND HISTORY

2.1 Site Selection

In consultation with the USAEC and the USACE, it was decided to obtain lead-contaminated soil from an explosives burning ground located at the SFAAP in Desoto, Kansas. Site selection was based on three major criteria:

- Lead-contamination at the site was ionic in nature; therefore, the soil could be treated using phytoextraction techniques.
- Contaminant depth was less than one foot; therefore, the plant root structures could access the contaminates if the site were chosen for remediation.
- The area showed textural differences in the soil. (For demonstration purposes, testing with two or more soil textures was considered desirable.)

2.2 Location of the Sunflower Army Ammunition Plant

The SFAAP is located approximately 30 miles southwest of Kansas City, Kansas, and 16 miles east of Lawrence, Kansas, along Route 10. The SFAAP encompasses about 10,000 acres and is located south of DeSoto, Kansas, in the northwest corner of Johnson County (Figure 2-1). The area immediately surrounding SFAAP is a sparsely populated area composed of privately owned agricultural lands. The plant is bounded on the east by the Spoon and Kill Creeks and on the west by Captains Creek. The Kansas River is located approximately three miles north of the plant.

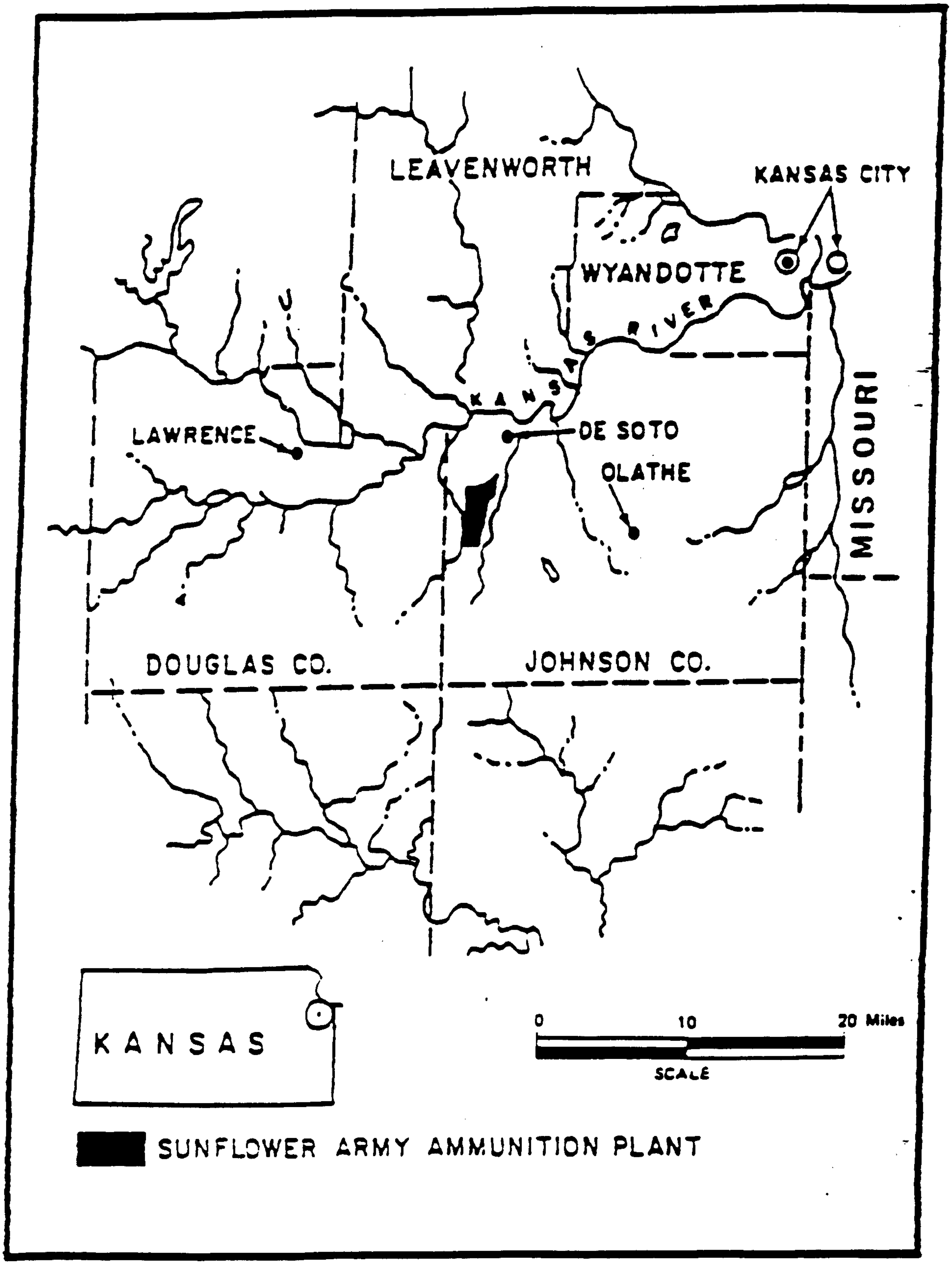


Figure 2-1

Location of the Sunflower Army Ammunition Plant

2.3 History of the Sunflower Army Ammunition Plant

The SFAAP is a government-owned contractor-operated facility which has intermittently manufactured smokeless powder, propellants, and related products since the early 1940s. The plant's production history is summarized in Table 2-1.

SFAAP began to produce propellants and related products in 1943. Over the years, three base explosives have been produced for incorporation into propellants: nitroglycerin (NG), nitrocellulose (NC), and nitroguanidine (NQ). The propellants manufactured at SFAAP contained one or more of the three base explosives, a stabilizer, a plasticizer, extrusion lubricant, and generally two burning rate modifiers. Among the propellants produced was N-5, a rocket propellant consisting of a mixture of organic and lead-organic compounds.

In addition to the base explosives, nitric and sulfuric acids were manufactured at the plant. These acids are required to produce the organic nitrates and calcium cyanamide, the major raw material used in the NQ production process. The NG, NC, and acid production areas have long been operated at SFAAP, whereas NQ and calcium cyanamide production did not begin until the late 1970s. Processes involved in the propellant production included: mixing, washing, air drying, blending, rolling, pressing, annealing, fluoroscoping, milling, and trimming. Support functions for the production processes included product testing and storage, water and steam production, waste treatment, and facility maintenance.

Recent activities at SFAAP have occurred at the acid area facilities, continuous paste facility, mechanized roll (solventless roll) complexes, and the NG facility. The NQ facility was shut down on September 1, 1992, and has been put into "standby" status.

2.4 Description of the Lead-Contaminated Site at SFAAP

The soil sampling and soil excavation activities were conducted on an explosives burning ground located within the SFAAP. The explosives burning ground consists of five approximately 1-acre "cells" plus additional outlying areas of approximately 7-10 acres. Lead contamination in the burning grounds originated from the burning of N-5 propellant, a mixture of organic and lead-organic compounds. N-5 rocket propellant was produced at SFAAP from

Table 2-1

Sunflower APP's Production History

Year	Event
1942	Construction began.
1943	Production began.
1943-1948	Propellant produced - including lead-bearing propellants.
1948-1951	Standby maintenance; ammonium nitrate liquor and NC production continued while a majority of plant was inactive.
1951-1960	Propellant produced - including lead-bearing propellants.
1960-1965	Standby maintenance; sulfuric acid production continued while majority of plant was inactive.
1966-1971	Propellant produced - including lead-bearing propellants.
1971-1977	Standby maintenance.
1977-1992	NQ and calcium cyanamide produced.
1992-present	NQ facility in standby mode.

1943 to 1971. The range of lead contamination over the burning area is 10-15,800 mg/kg. Other heavy metals are also present in varying concentrations.

Two sites were selected for soil sampling; one site located in Cell 1 and the other in the northern-most outlying area. The northern-most area has been designated as Cell 7 for the purposes of this plan (Figure 2-2). Cell 7 is within 850 feet of the northern-most arm of a flowing creek (Captains Creek), while Cell 1 is approximately 1,500 feet distant to the south. Both cells are located on a sloping, grassy meadow.

The soil is generally classified as Kennebec alluvial silt loam, although there are distinct textural differences ranging from the silt loam to a silty clay. Previous physical analyses show the soil in Cell 1 to be an alluvial silty clay (50% silt, 50% clay) and the soil in Cell 7 to be an alluvial silt loam (60% silt, 25% sand, and 15% clay). (Data obtained by correspondence with USACE.) There is sufficient distance between cells that there is a distinct difference in textural classification in the soil. Thus, for the purpose of this project, the soil may be considered as being of two distinct types.

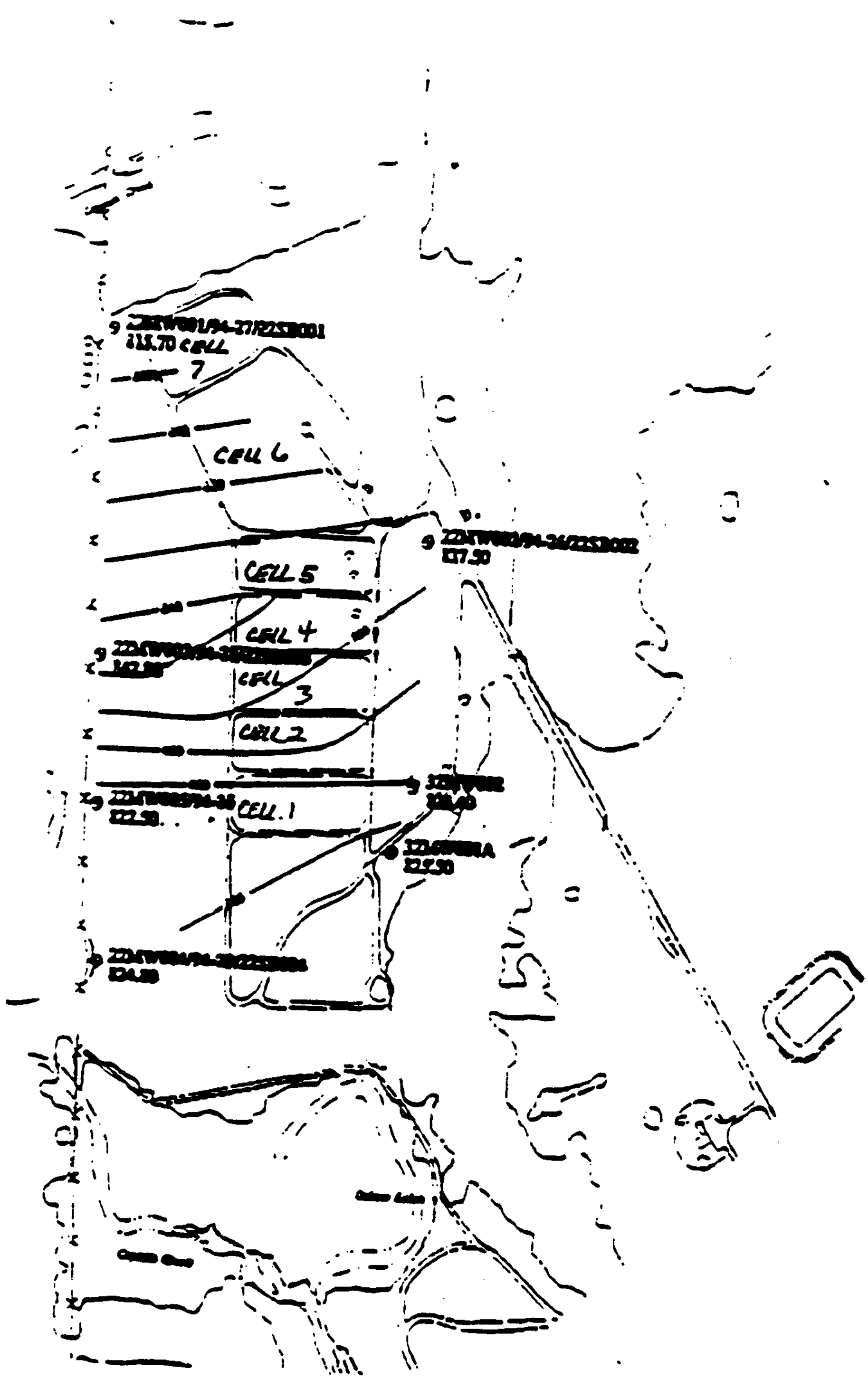


Figure 2-2

Location of Cells 1 and 7 at the SFAAP

SECTION 3.0
TECHNOLOGY DESCRIPTION

3.1 Waste and Media Application

Phytoextraction is an *in situ* remediation method which uses plants to remove ionic metals from contaminated soils. Ionic metals are commonly produced when metal-containing propellants, explosives, and powders are burned on soil-bearing strata. Ionic lead contamination may also occur when leaded chemicals or fuels are spilled. Particulate lead, bullet fragments for example, cannot be treated by this process. Phytoextraction methods may be used to treat lead concentrations in the 3,000-4,000 ppm range. The lead concentrations are reduced by 200 to 700 mg lead/kg soil per year.[Ref. 2] Remediation at higher concentrations is technically feasible but would require a longer time frame.

3.2 Current Practice and Alternatives

Several procedures for remediating metal-contaminated soil sites are currently available. These include:

- Landfilling contaminated soil.
- Soil washing (separation) - soil excavation followed by soil washing, returning the clean soil to the site, and landfilling the contaminated soil.
- *In situ* soil flushing - in-place soil washing using acid or chelate solutions followed by recovery of the contaminated leachates and surface treatment of the leachates.
- Containment - placing a cap on contaminated sites to eliminate water infiltration.
- Phytoextraction - plant species are used to extract heavy metals from the soil and are then harvested.

These technologies, except containment, provide a clean site and normally avoid restrictions to site use. Currently, the lowest cost option is phytoextraction (Table 3-1).

Table 3-1

Comparison of Remediation Costs

Remediation Method	**Cost of Remediation Technique ($ per cubic yard)**
Phytoextraction	$25 - $124 [Refs. ,3]
Containment	$100 - $175 [Ref. 4]
Landfilling	$165 - $410 [Refs. 1,3]
Soil washing	$175 - $390 [Ref. 4]
In situ soil flushing	$300 - $380 [Ref. 4]

3.3 Technology Description

In phytoextraction, heavy metals accumulate in the plant shoot tissues in sufficient concentrations to cause plant death. After the plants die, the shoots are harvested and can either be processed for metals recovery or be disposed of as a hazardous waste. In contrast to other remediation methods, phytoextraction techniques allow for *in situ* metals extraction and recovery; mechanical soil removal is not necessary.

The plant extraction of ionic lead is the primary focus of this technology. However, lead is not easily removed from soil and taken up by plants. Lead is considered the least soluble and least mobile of the heavy metals. Ionic lead is usually present in soil as insoluble salts or solid phase compounds which are not easily dissolved in soil solution (i.e., lead carbonate, lead cerussite, etc.), thus its availability to plants is generally low. Lead also tends to accumulate within most plant root structures rather than moving to the aerial shoots.[Ref. 5] Before being taken up by a plant, lead solid phases (lead-containing minerals and salts) have to be dissolved into the soil solution as ionic lead (Pb^{2+}) through the use of soil amendments such as acidifiers and chelates. Upon dissolution, Pb^{2+} is released into the soil solution, absorbed into the plant roots, and translocated to the plant shoots.

A plant's capacity to take up lead can be enhanced by adding soil amendments to increase lead solubility. Solubilization increases the availability of soil-borne lead for plant uptake. Treatment with soil amendments also increases the translocation of lead to the above ground portions of the plant and lead accumulates in the shoot at much higher concentrations than without solubilization. Amendment use allows lead accumulation of up to 2% in the aboveground portions of selected plant species.

Soil amendments currently used for phytoextraction are soil acidifiers and chelates. Soil acidifiers, such as acetic acid, temporarily increase soil acidity, thereby causing lead solubilization. Chelates, such as ethylene-dinitrilo-tetraacetic acid (EDTA), enhance the solid phase solubilization by chelating solution-borne lead, thus shifting the equilibrium toward dissolution (i.e., lead ions combine with the chelating agent, thereby removing lead from the liquid phase and promoting additional release of the solid phase into the liquid phase). Chelation may be viewed as the multiple bonding of a metal to coordinating groups of an organic compound to form a stable charge structure.

There are several components to a phytoextraction scheme. A lead phytoextraction "processing unit" consists of a plowed field containing the contaminated soil, a crop, irrigation system, fence, farm equipment, decontamination equipment, personal protective equipment, and a decontamination area. The field should be fenced to prevent wildlife intrusion onto the field. The decontamination area is used to facilitate the decontamination of personnel and farm equipment leaving the contaminated field. Depending upon the local climate, one or more crops may be grown during any given year. Plant species that have shown suitable characteristics for lead remediation with application of soil amendments are corn, alfalfa, Indian mustard, white mustard, sorghum sudan grass, and sunflower.

To "operate" the field, a crop which is adapted to the local climate is planted and grown to full vegetative biomass maturity (i.e., to a stage just before fruit or grain production) using common farm practices. After the plants have matured, amendments are added to the soil to promote lead solubilization. Within a few days, the plants begin to senesce (die) due to the increased lead uptake. After the crop has died, the plant shoots are harvested using common farming techniques or by hand. The harvested crop is then either processed for metals

recovery (smelted) or sent to a hazardous waste disposal site. When possible, a cover crop may be grown in the winter season to control wind and water erosion. The cover crop is tilled back into the soil prior to planting the spring crop. Common cover crops include wheat, barley, and annual ryegrass.

3.4 Advantages and Limitations

The feasibility of implementing a phytoextraction program at a particular site is influenced by:

- The soil lead content
- The underlying geology
- The potential for phosphorus deficiencies in the soil
- Local weather conditions
- Plant selection

Sites with soil lead concentrations less than 3,000 to 4,000 mg ionic lead/kg soil are the most suitable for phytoextraction, since this type of site could be remediated within several years. Plants may be used to remediate soil with lead concentrations greater than 3,000 to 4,000 ionic mg lead/kg soil without interfering with plant growth. However, the expected reduction in soil lead ranges from 200 to 700 mg lead/kg soil per year, so the time required to complete a remediation program may become unrealistic for higher concentrations.[Ref. 2]

The underlying geology may also be a concern. Because soil amendments increase lead solubility, lead may leach from the plant root zone into lower soil layers, adjoining areas, or groundwater. Therefore, careful attention must be paid to the hydraulic conductivity of the underlying geology, as well as the levels of soil amendment application.

Phosphorus-deficient soils are also a factor. Lead-contaminated soils tend to be deficient in plant-available phosphorus (P) because lead precipitates P as insoluble lead-phosphate complexes. The manifestations of phosphorus deficiency include decreased plant growth and decreased biomass accumulation. Phosphorus deficiency lowers remediation effectiveness by reducing total lead uptake.[ref. 6] This can be remedied by supplying additional P to the plant, either by foliar application (i.e., spraying a water-soluble phosphate fertilizer solution directly

on the plant) or by banding (i.e., applying bands of phosphate fertilizer below the soil surface and to the side of the plant or seed row).

Local weather conditions affect growing season length, crop type, and crop sequence. In turn, the types of plants to be grown at a site are subject to evaluation for a number of considerations including: growing season length, adaptability to local conditions, soil fertility, and ability to take up lead. Suitable candidates for warm season crops are corn (*Zea mays* L.), sunflower (*Helianthus annus* L.), and sorghum sudan grass (*Sorghum sudanense* L.). White mustard (*Brassica hirta* L.), Indian mustard (*Brassica juncea* L.), alfalfa (*Medicago sativa* L.) appear to be suitable cool season crops.

Relative to other remediation technologies, phytoextraction methods have a number of advantages. These include:

- Low remediation cost range from $25 to $127 per cubic yard (see Table 3-1).
- Heavy metals removal by plant harvesting minimizes site disturbance and limits contaminant dispersal.
- Heavy metals recycling is possible via the processing (smelting) of the harvested plant tissues.
- If the heavy metals are recycled, the cost and long-term liability associated with maintaining a landfilled hazardous waste is substantially reduced or eliminated.
- Operating space requirements are limited to the field being treated.
- The technology is relatively simple and easy to implement.

3.5 Current Status

Currently, phytoextraction techniques are being investigated for potential use at DoD sites. In the mid-1990s, the USAEC became interested in phytoextraction methods after private-sector laboratory studies and field trials suggested that the technique could become a cost-efficient means of remediating metals-contaminated soils (Tables 3-2 and 3-3).

In 1997, the USAEC funded this project to determine whether the effectiveness of phytoextraction techniques could be increased. The preliminary results were sufficiently encouraging that the ESTCP funded a field demonstration of the phytoextraction technique beginning in spring of 1998. The field demonstration facility is being conducted at the Twin Cities Army Ammunition Plant (TCAAP) at Arden Hills, Minnesota.

Table 3-2

List of Promising Research with Synopsis of Findings

- In greenhouse pot tests, translocation of lead from roots to shoots in corn plants increased 120-fold within 24 hours of a soil application of 1,000 mg/kg EDTA.[ref. 6]
- In laboratory pot trials with addition of chelates to soil, shoot lead concentrations have reached 1% lead in corn and peas.[ref. 7]
- Corn exposed to low lead concentrations (4 ppm) in hydroponic solutions accumulated 0.2% lead in shoots.[ref. 8].
- Cultivars of Indian mustard selected for lead uptake using hydroponic solutions or sand/perlite mixtures for growth and lead application accumulated up to 3.5% lead in shoots.[ref. 9]

Table 3-3

List of Known Phytoextraction Field Trials with Synopsis of Findings

- Bayonne, New Jersey, site: Soil at a Texaco Oil site contaminated with 1,000 ppm lead is being remediated using the plant species Indian mustard with soil amendments of the chelate EDTA alone and EDTA in combination with acetic acid to lower soil pH. Lead concentrations in plant shoots have attained 0.4%. Remediation is estimated to require two to three years. [No published data - discussion by Dr. I. Raskin at Phytoremediation Conference, Alabama A&M Univv. [ref. 10]]

- Palmerton, Pennsylvania, site: A Superfund site contaminated with 2,000 to 50,000 ppm zinc and 38 to 1,020 ppm cadmium is being used to assess the effectiveness of the species Alpine pennycrest (*Thlaspi caerulescens*), in conjunction with soil amendments to acidify the soil, to remove soil contaminants.[ref.11] Zinc concentrations in Alpine pennycrest shoots from the field site were 0.6 to 1.0% (R. Chaney, personal communication). In greenhouse studies using soil from the Palmerton site, Alpine pennycrest accumulated 1.8% zinc and 0.1% cadmium in the shoots without yield reduction associated with metals toxicity.[ref.11]

- Liberty Park, New Jersey, site: Soil contaminated with chromium is being remediated by planting with Indian mustard.[ref.1]

- Trenton, New Jersey, site: A Brownfield industrial site formerly used for the manufacture of Magic Marker pens and batteries had soil contaminated with 927 ppm lead and was remediated with chelating agents and a crop of Indian mustard. Cleanup was almost complete in one summer and sampling of the plot down to 45 cm six months after application of 3,000 mg/kg EDTA indicated no significant leaching of the chelate below 15 cm.[ref. 12]

- Butte, Montana, site: The DOE began large plot field tests in 1997 to determine uptake capacity of several *Brassica* varieties (Indian mustard, rape, turnip) and grasses for cadmium, zinc, and radioactive cesium and strontium.[ref. 13]

- Superfund Innovative Technology Evaluation Program site in Ohio: A field demonstration is in progress on soil at a former metal plating facility to evaluate phytoextraction of cadmium, lead, and hexavalent chromium by Indian mustard. The demonstration was initiated in 1996 and includes monitoring the soil, groundwater, and plant material until at least 1999. To date, there has been no downward movement of lead through the soil profile.[ref. 14]

SECTION 4.0
EXPERIMENTAL DESIGN

4.1 Introduction

This project was executed to refine the use of chelates in phytoextraction through laboratory and greenhouse studies. Two preliminary laboratory studies evaluated chelate effectiveness and persistence in soil. Six greenhouse studies tested plant species for their effectiveness in removing lead from two contaminated soils which differ in chemical and physical properties, and the movement of chelates and lead in the contaminated soils.

4.2 Approach

The work involved plant selection, process optimization, and treatability studies in the laboratory and greenhouse to achieve the greatest lead removal from two lead-contaminated soils having contrasting chemical and physical properties. The soils were collected from a DoD-owned explosives burning ground (SFAAP) and brought to TVA's Greenhouse facility in Muscle Shoals, Alabama, where the soil was processed and the studies performed.

The principles of chelation chemistry were used as the basis for the project (see Section 3.3). During this project, the soil was adjusted to a given pH to enhance lead dissolution from the solid phase and a chelating agent added to the soil to bind with the lead and keep it in solution. Calculations based on competitive metal/chelate equilibria were used to determine the theoretical maximum amount of chelate required to complex and solubilize all of the lead at a given pH. However this was only an approximation, since these calculations were based on pure systems which contain no other competing ligands that might complex with lead and no other metals that would complex with the ligand. Ideally, the amount of chelate used would only complex the amount of lead the plants can assimilate. In an attempt to avoid using excess chelate, the chelate was added to the soil in molar ratios (chelate/soil-borne lead) of 0.5, 1.0, and 1.5.

4.3 Soil Characterization, Collection, and Processing

Prior to beginning the studies, the USAEC, USACE, and TVA selected two sites at SFAAP which contained suitably contaminated soil with which to conduct this project. The soil from these two sites was collected and analyzed to characterize lead concentrations in the immediate area. The soil was then excavated and shipped to TVA's Environmental Research Center (ERC) in Muscle Shoals, Alabama, for use during this project.

During the soil characterization phase, each site was subdivided into 36 fifteen-foot grids and then sampled using a hand-held soil probe. One hundred and forty four (144) soil samples were taken from the sites (36 grids/site X 2 sample depths/gird X 2 sites = 144 soil samples) and shipped to the TVA ERC for analysis. The samples were analyzed for pH and total lead (Table 4-1).

After the sampling sites were properly mapped, 1,000 kg of bulk soil with lead concentrations in the desired range (3,000 to 4,000 mg/kg) was collected from each site and shipped to the ERC in Muscle Shoals, Alabama (see excavation procedure in Appendix D-2). The soil was processed by passing it through a gasoline-powered soil shredder/screen. The soil was then thoroughly mixed to homogenize it. Twelve soil samples were taken from the soil mixture and the soil was rebarreled and stored. The soil samples obtained during this process were used to determine the chemical characteristics and nutrient content of the soil (Table 4-2). This data was used to establish a baseline for the studies to follow and as a screening mechanism to determine the amount of lead (Pb), cadmium (Cd), copper (Cu), molybdenum (Mo), nickel (Ni), zinc (Zn), chromium (Cr), mercury (Hg), and selenium (Se) in the soil. The lead and pH data is provided in Appendix F.

4.4 Description of Preliminary Laboratory Studies

4.4.1 Chelate Screening Study

Chelate efficiency was evaluated during the Chelate Screening Study. To accomplish this, different chelates at varying concentrations were used to solubilize metals at different soil pH levels. An overview of the Chelate Screening Study experimental design is provided in

Table 4-1

Chemical Analyses for the Soil Characterization/Mapping Work

Sample Type	Minimum Sample Size[1]	Parameter Measured
Soil	12 grams	pH Total Metals (Pb)[2]

(1) Every tenth sample contained twice the usual amount of sample and was submitted for use in the QA/QC program.

(2) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and was used to distinguish it from metals measured following a leaching process.

Table 4-2

Chemical Analyses for Bulk Soil Sampling

Sample Type	Minimum Sample Size[1]	Parameter Measured
Soil	60 grams	pH Buffer Curves
		Cation Exchange Capacity (CEC)
		Field Capacity
		Total Organic Carbon (TOC)
		Total Kjeldahl Nitrogen (TKN)
		Extractable P
		Exchangeable K
		Exchangeable Ca
		Exchangeable Mg
		Exchangeable Al
		DTPA-Extractable Fe
		DTPA-Extractable Mn
		Total Metals (Pb, Cd, Cu, Mo, Ni, Zn, Cr)[2]
		Total Metals (Hg)[2]
		Total Metals (Se)[2]
		EDTA-Soluble Pb
		Plant-Available Pb

(1) Every tenth sample contained twice the usual amount of sample and was submitted for use in the QA/QC program.

(2) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and was used to distinguish it from metals measured following a leaching process.

Table 4-3 and details of the experimental design are provided in Table 4-4. A listing of the chemical analyses performed are provided in Table 4-5.

Various soil components can alter a chelate's ability to complex specific metals due to competing ion effects. For example, lowering soil pH will, in most cases, increase the amount of metal in the soil solution. This occurs because protons (hydrogen ions) compete with metals for exchange sites on clay micelles and organic components in the soil or because some inorganic constituents are soluble at lower pH. Metals which are unable to bind to an exchange site may be complexed by a chelate. Any metals which react with the chelate become more water-soluble and are, therefore, more readily taken up by plants.

This study was conducted at the natural soil pH (pH 7.0 to 7.3) and at a pH of 5.5, where lead solubility is higher. To determine the amount of acetic acid required to lower the soil pH to 5.5, acetic acid was applied to 100 g subsamples of bulk soil at concentrations of 0.03, 0.04, 0.05, and 0.06 millequivalents (meq) of acetic acid per gram of soil. The soil pH was monitored over a 72-hour period since these soils tend to buffer the pH over time.

Three chelates were selected for study:

- Ethylenedinitrilotetraacetic acid (EDTA)
- Cyclohexane - 1,2 - Diaminetetraacetic Acid (CDTA)
- Ethylene bis(oxyethylenetrinitrlo)tetraacetic acid (EGTA)

The chelates were applied to 100-g soil samples at concentrations of 0.15, 1.5, and 15 mmole of chelate/kg soil, both at the natural soil pH and at a pH of 5.5. The chelate and acetic acid soil amendments were applied in sufficient water to bring the 100-g soil samples to field capacity. The water was added slowly to prevent dispersion and mixing of soil since the soils exhibited very slow infiltration rates. The term "field capacity" refers to the amount of water a soil can hold. The volume of solution added was sufficient to percolate through the entire volume of soil. Testing indicated that the soil field capacity of both soils was 32%

Table 4-3

An Overview of Experimental Designs for the Preliminary Laboratory Studies

Chelate Screening Study

3 Chelates

3 Chelate concentrations

2 soil pH levels

2 soils

plus

2 controls

20 treatments replicated 3 times for each soil

Total: 120 units, 120 samples

Chelate Applications Study

1 cropping system (planted)

1 chelate level

2 volumes of water for chelate application

3 time periods

2 soils

2 replicates

4 depths

Total: 24 units, 96 samples

Table 4-4

Experimental Design Details for the Chelate Screening Study

Soil Source	Chelate Type	pH	Chelate Concentration (mmole/kg soil)	Number of Replicates	Chemical Analyses	Number of Soil Samples
Cell 1	EDTA	Natural	0.15, 1.5, &15	3	See Table 4-5	9
Cell 1	EDTA	pH 5.5	0.15, 1.5, &15	3	See Table 4-5	9
Cell 1	EGTA	Natural	0.15, 1.5, &15	3	See Table 4-5	9
Cell 1	EGTA	pH 5.5	0.15, 1.5, &15	3	See Table 4-5	9
Cell 1	CDTA	Natural	0.15, 1.5, &15	3	See Table 4-5	9
Cell 1	CDTA	pH 5.5	0.15, 1.5, &15	3	See Table 4-5	9
Cell 1	None (Control)	Natural	0	3	See Table 4-5	3
Cell 1	None (Control)	pH 5.5	0	3	See Table 4-5	3
					Total	60
Cell 7	EDTA	Natural	0.15, 1.5, &15	3	See Table 4-5	9
Cell 7	EDTA	pH 5.5	0.15, 1.5, &15	3	See Table 4-5	9
Cell 7	EGTA	Natural	0.15, 1.5, &15	3	See Table 4-5	9
Cell 7	EGTA	pH 5.5	0.15, 1.5, &15	3	See Table 4-5	9
Cell 7	CDTA	Natural	0.15, 1.5, &15	3	See Table 4-5	9
Cell 7	CDTA	pH 5.5	0.15, 1.5, &15	3	See Table 4-5	9
Cell 7	None (Control)	Natural	0	3	See Table 4-5	3
Cell 7	None (Control)	pH 5.5	0	3	See Table 4-5	3
					Total	60
					Grand Total	120

Table 4-5

Chemical Analyses for the Chelate Screening Study

Sample Type	Minimum Sample Size[1]	Preservative Added	Parameter Measured
Soil	10 grams	None	pH
Water Extract	50 ml	Filtered[2] then Nitric Acid added Until pH<2	Total Dissolved Metals (Pb, Cd, Cu, Ni, Zn, Cr)

(1) Every tenth sample contained twice the usual amount of sample and was submitted for use in the QA/QC program.

(2) Filtered through Whatman #2 or equivalent.

moisture by weight. The soil and amendments were allowed to reach equilibrium over a 24-hour period. A subsample of the soil was then extracted with water and analyzed to determine chelate efficiency at solubilizing lead at that pH.

The chelate most effective at promoting lead solubility during the Chelate Screening Study (EDTA) was used in the Chelate Applications Study and all subsequent greenhouse studies. The basis for determining the most effective chelate is described in Section 5.2.1

4.4.2 Chelate Applications Study

Excess chelates applied to contaminated soils may create a metals leaching problem, since lead could be leached below treatable depths if the chelate moves down past the root zone. This could occur if too much solution is added during soil amendment application or if residual chelates are flushed out of the root zone after harvest. The Chelate Application Study was designed to:

- Determine the amount of water applied with the chelate
- Test chelate persistence in soil

An overview of this study's experimental design is provided in Table 4-3, and details of the experimental design are provided in Table 4-6.

The study was conducted in 2-inch diameter 24-inch long PVC columns. Each column contained approximately 1.6 kg of soil and was planted with Indian mustard (*Brassica juncea* L.). Indian mustard was used because prior research indicated it was the most effective of the species that take up lead[Ref. 9] and this project's plant selection process had not been completed. When the plants reached full vegetative biomass, EDTA was added to the columns as a water solution. The EDTA was applied in sufficient water to bring the whole soil column to either field capacity or 1.5 times field capacity. Soil pH was not adjusted during this study.

After applying the EDTA, the soil in each column was sampled at three time periods to determine the movement and persistence of EDTA in the soil. Sampling times used for the soil from Cell 1 were 2, 7, and 14 days. Sampling times for the soil from Cell 7 were 7, 14, and

Table 4-6

Experimental Design Details for the Chelate Applications Study

Soil Source	Crop	Chelate Amount	Volume of Water for Chelate Application	Time Periods	Number of Replicates	Sampling Soil Depths	Chemical Analyses	Number of Soil Samples
Cell 1	Indian Mustard	16.7 mmoles	1.0 X FC[1]	2 Days	2	4	See Table 4-7	8
Cell 1	Indian Mustard	16.7 mmoles	1.0 X FC[1]	7 Days	2	4	See Table 4-7	8
Cell 1	Indian Mustard	16.7 mmoles	1.0 X FC[1]	14 Days	2	4	See Table 4-7	8
Cell 1	Indian Mustard	16.7 mmoles	1.5 X FC[1]	2 Days	2	4	See Table 4-7	8
Cell 1	Indian Mustard	16.7 mmoles	1.5 X FC[1]	7 Days	2	4	See Table 4-7	8
Cell 1	Indian Mustard	16.7 mmoles	1.5 X FC[1]	14 Days	2	4	See Table 4-7	8
							Total	48
Cell 7	Indian Mustard	20.0 mmoles	1.0 X FC[1]	7 Days	2	4	See Table 4-7	10
Cell 7	Indian Mustard	20.0 mmoles	1.0 X FC[1]	14 Days	2	4	See Table 4-7	10
Cell 7	Indian Mustard	20.0 mmoles	1.0 X FC[1]	28 Days	2	4	See Table 4-7	10
Cell 7	Indian Mustard	48.2 mmoles	1.5 X FC[1]	7 Days	2	4	See Table 4-7	10
Cell 7	Indian Mustard	48.2 mmoles	1.5 X FC[1]	14 Days	2	4	See Table 4-7	10
Cell 7	Indian Mustard	48.2 mmoles	1.5 X FC[1]	28 Days	2	4	See Table 4-7	10
							Total	48
							Grand Total	96

(1) FC - Field capacity of the soil.

28 days, with the sampling times extended to determine whether EDTA concentrations in soil would change over a longer time period.

To investigate the use of different application methods, EDTA was applied differently to each soil. The EDTA added to Cell 1 soil was applied at a molar EDTA-to-lead ratio of 1.0 (16.7 mmoles per column) at field capacities of 1.0 and 1.5. This was accomplished by adjusting the EDTA concentration applied. The EDTA added to Cell 7 soil was applied at a fixed concentration, consequently, the amount of EDTA added to each column varied with the amount of solution applied (20 mmole per column at a field capacity of 1.0 and 48.2 mmoles per column at a field capacity of 1.5).

During each sampling period, the soil samples were obtained at depths of 0"-6", 6"-12", 12"-18", and 18"-24". The soil samples were analyzed for pH, total lead, plant-available lead (i.e., water-soluble lead), chelates, and moisture (Table 4-7).

4.5 <u>Greenhouse Studies</u>

The greenhouse studies consisted of:

1) A Plant Screening Study to determine which warm and cool season plants would optimize lead removal, the amount of EDTA to add, and if the soil needed to be acidified to optimize lead removal.

2) A Foliar Application Study to determine the optimal level of foliarly applied phosphate needed to decrease lead toxicity and to enhance biomass growth.

3) Soil Leaching Study to determine the extent of EDTA movement through soil columns and whether lead will leach out of the root zone as a result of solubilization by EDTA.

4) Lysimeter Study which was similar to the Soil Leaching Study, but which included collection of soil solution at various depths using suction lysimeters.

Table 4-7

Chemical Analyses for the Chelate Applications Study

Sample Type	Minimum Sample Size[1]	Parameter Measured
Soil	50 grams	pH Total Metals (Pb)[2] Plant-Available Pb Chelates Moisture

(1) Every tenth sample contained twice the usual amount of sample and was submitted for use in the QA/QC program.

(2) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and is used to distinguish it from metals measured following a leaching process.

5) A Chelate Application Timing Study to determine the optimum time for adding the EDTA chelate to the selected cool season crop. (The resultant cool season crop, white mustard, takes up water at a more rapid rate during bolting and flowering. Thus, a properly timed application could increase lead uptake.)

6) A Harvest Timing Study to determine the time required for maximum lead uptake by white mustard after EDTA addition.

An overview of the experimental designs for these studies is provided in Table 4-8.

The Foliar Application Study was conducted using 5-inch diameter 8-inch deep plastic pots containing 2 kg of soil. The Chelate Application Timing Study and the Harvest Timing Study were conducted in 4-inch diameter 4-inch deep plastic pots containing 1 kg of soil.

4.5.1 Plant Screening Study

The Plant Screening Study was designed to determine:

- The amount of lead that six pre-selected plants species would take up and translocate to their shoots
- The amount of EDTA to add to each soil type
- If the soils needed to be acidified to optimize lead removal

The plants studied were selected on the basis of their ability to produce high levels of biomass and grow in climates like that of a proposed field demonstration site at TCAAP. Six plant species were screened for lead uptake efficiency:

- Indian mustard (*Brassica juncea* L.)
- White mustard (*Brassica hirta* L.)
- Corn (*Zea mays* L.)
- Sorghum sudan grass (*Sorghum sudanense* L.)

Table 4-8

An Overview of Experimental Designs for the Greenhouse Studies

<u>Plant Screening Study</u>

2 soil types (Cell 1 and Cell 7 soil)

6 plant species

4 chelate levels

2 soil pH levels

3 replicates

<u>Total:</u> <u>288 pots</u>

<u>Foliar Application Study</u>

2 soil types (Cell 1 and Cell 7 soil)

2 best plant species (corn and white mustard)

3 phosphate levels

3 replicates

<u>Total:</u> <u>36 pots</u>

<u>Soil Leaching Study</u>

2 best treatments (corn at soil pH 5.5 and a molar EDTA-to-lead ratio of 1.0; white mustard at the natural soil pH and molar EDTA-to-lead ratio of 1.0)

2 soil types (Cell 1 and Cell 7 soil)

2 replicates for each combination of treatments by soil type

<u>plus</u> 4 controls (1 of each soil and species)

<u>Total:</u> <u>12 containers</u>

Replanting:

2 species (corn and white mustard)

2 soil types

1 treatment

<u>Total:</u> <u>4 containers</u>

Table 4-8 (Continued)

An Overview of Experimental Designs for the Greenhouse Studies

Lysimeter Column Study

1 species (white mustard)

1 soil type (Cell 7 soil)

1 treatment

2 replicates

Total: 2 containers

Chelate Application Timing Study

1 treatment

1 soil type (Cell 7 soil)

1 species (white mustard)

2 time periods for chelate application

3 replicates

Total: 6 pots

Harvest Timing Study

1 treatment

1 soil type (Cell 7 soil)

1 species (white mustard)

5 harvest times

3 replicates

Total: 15 pots

- Alfalfa (*Medicago sativa* L.)
- Sunflower (*Helianthus annus* L.)

The plants consisted of four broad-leafed dicotyledons (alfalfa, Indian mustard, white mustard, and sunflower) and two tropical grass monocotyledons (corn and sorghum sudan). The plants were further subdivided into cool season species (Indian mustard, white mustard, and alfalfa) and warm season species (corn, sorghum sudan grass, and sunflower).

The treatment parameters (soil type, soil pH, and chelate concentration) were varied during the study to:

- Determine the conditions for optimum lead uptake by each plant species.
- Provide a basis for determining which plant would be the most suitable for commercial use.

Treatment parameters varied during the study included:

- Two soil types (a silty clay from Cell 1 and a silt loam from Cell 7)
- Soil pH (natural pH or pH 5.5)
- The molar ratio of EDTA-to-soil lead. (Four EDTA/Lead ratios were examined: 0, 0.5, 1.0, and 1.5).

Details of the Plant Screening Study experimental design are provided in Table 4-9. A listing of the chemical analyses performed are provided in Table 4-10.

Each of the six crops was grown from seed in 8-inch diameter 12-inch deep plastic pots containing 4 kg of soil. A total of 288 pots were used during the study (6 crops x 2 soil types x 2 soil pH x 4 EDTA-to-lead ratios x 3 replicates = 288 pots).

During the planting process, each crop received sufficient fertilizer to satisfy its optimum fertilization rates for nitrogen and potassium. Phosphate fertilizers were not added. Soil nutrient analyses obtained during the Soil Characterization Study (Table 4-1) were used to determine the nutrient content of each soil and to calculate the soil fertilization rates.

Table 4-9

Experimental Design Details for the Plant Screening Study

Soil Source	Crop	Ratio of EDTA to Lead in Soil (Mole EDTA/Mole Pb)	Soil pH	Number of Replicates	Chemical Analyses	Number of Soil Samples[1]	Number of Aerial Plant Samples[2]
Cell 1	Indian Mustard	Four ratios (0.0, 0.5, 1.0, 1.5)	Natural & pH 5.5	3	See Table 4-10	24	24
Cell 1	White Mustard	Same as above	Same as above	3	See Table 4-10	24	24
Cell 1	Corn	Same as above	Same as above	3	See Table 4-10	0	24
Cell 1	Sorghum sudan grass	Same as above	Same as above	3	See Table 4-10	0	24
Cell 1	Alfalfa	Same as above	Same as above	3	See Table 4-10	24	24
Cell 1	Sunflower	Same as above	Same as above	3	See Table 4-10	0	24
					Total	72	144
Cell 7	Indian Mustard	Four ratios (0.0, 0.5, 1.0, 1.5)	Natural & pH 5.5	3	See Table 4-10	24	24
Cell 7	White Mustard	Same as above	Same as above	3	See Table 4-10	24	24
Cell 7	Corn	Same as above	Same as above	3	See Table 4-10	0	24
Cell 7	Sorghum sudan grass	Same as above	Same as above	3	See Table 4-10	0	24
Cell 7	Alfalfa	Same as above	Same as above	3	See Table 4-10	24	24
Cell 7	Sunflower	Same as above	Same as above	3	See Table 4-10	0	24
					Total	72	144
					Grand Total	144	288

(1) Soil samples taken post-harvest.
(2) Aerial plant samples taken at harvest.

Table 4-10

Chemical Analyses for the Plant Screening Study

Sample Type	Minimum Sample Size[1]	Parameter Measured
Soil	7 grams	Plant-available Pb[2]
Plant (aerial: control groups)[3]	4 grams	Total Metals (Pb)[4] Total P[3]
Plant (aerial: all others)	2 grams	Total Metals (Pb)[4]

(1) Every tenth sample contained twice the usual amount of sample and was submitted for use in the QA/QC programs.

(2) Only soils containing cool season plant species were analyzed for plant-available lead. Soil containing warm season plant species were not analyzed because literature sources indicated that warm season species take up less plant-available lead than cool season species.

(3) Analyzed the "best" warm and cool season species (corn and white mustard) in the control group (the sample grouping with zero chelate concentration and natural soil pH). The basis for selecting the "best" species is described in Section 5.3.1. A total of six samples were obtained. The results were used during the Foliar Application Study to determine whether the existing soils are providing sufficient phosphorus to support growth (phosphorus content of 0.3-0.4% of the plant dry weight).

(4) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and is used to distinguish it from metals measured following a leaching process.

Throughout the study, the potted plants were placed in a randomized complete block design with each block containing all treatment variables, including soil type. Individual replicates within blocks were re-randomized each week. To ensure that nutrient deficiency did not limit plant growth, an additional fertilizer application was made midway through the growing season. To ensure each crop received an adequate amount of moisture, water was applied throughout the growing season as needed. The amount of moisture to be added was determined using moisture retention/release curves which had been developed for each soil type (Appendix C-5). The overall health of the plants was also monitored throughout the study.

When the plants reached full vegetative biomass, soil amendment treatments were applied to the pots, as indicated in Table 4-9. The plants senescenced (died) two to four days after the soil amendments were added. After the plants died, they were harvested, dried, weighed for biomass determination, ground, and analyzed for total lead content. In addition, an analysis for total P was run on the "best" warm and cool season species (corn and white mustard) in the control groups (groups with no added chelate). These analyses were used during the Foliar Application Study to determine whether the existing soils were providing sufficient phosphorus to support growth.

Post-harvest soil samples from soil in which cool season crops were grown were taken and analyzed for plant-available lead content. Plant-available lead and water-soluble lead are synonymous terms. The lead is "plant-available" because it is water-soluble and therefore may be taken up by the plant.

The best plant species and most effective soil treatment from this study were used in subsequent studies. The most effective treatment is defined here to mean the treatment leading to the highest level of lead uptake.

4.5.2 Foliar Application Study

Upon completing the Plant Screening Study, the Foliar Application Study was begun using the best warm and cool season crops (corn and white mustard) selected during the Plant Screening Study. During the Foliar Application Study, phosphate fertilizer was applied to the leaves of the plants to:

- Determine the best fertilization level for enhancing biomass growth
- Maximize lead uptake
- Reduce lead toxicity to the plants

The foliar application was expected to prevent formation of insoluble $Pb\text{-}PO_4$ complexes in the soil so that phosphate will not become unavailable to the plant. Details of the Foliar Application Study experimental design are provided in Table 4-11. A listing of the chemical analyses performed are provided in Table 4-12.

The experimental procedures for this study were essentially the same as those for the Plant Screening Study. The treatment variables were:

- Two plant species (corn and white mustard - the best plants from the Plant Screening Study)
- Two soil types (soils from Cells 1 and 7)
- Two soil pH (natural pH or pH 5.5)
- Three phosphate solution concentrations (solutions containing 0, 0.5, and 1.0% P)

Other parameters included:

- A 1.0 molar ratio of EDTA-to-soil lead
- Three replicates of each variable (plant species, soil type, soil pH, and phosphate solution concentration)

Table 4-11

Experimental Design Details for the Foliar Application Study

Soil Source	Crop	Ratio of EDTA to Lead in Soil (Mole EDTA/Mole Pb)	Soil pH	Phosphate Solution Concentration	Number of Replicates	Chemical Analyses	Number of Aerial Plant Samples[1]
Cell 1	Corn	1.0	5.5	0% (Control)	3	See Table 4-12	3
Cell 1	Corn	1.0	5.5	0.5 %	3	See Table 4-12	3
Cell 1	Corn	1.0	5.5	1 %	3	See Table 4-12	3
Cell 1	White Mustard	1.0	Natural	0% (Control)	3	See Table 4-12	3
Cell 1	White Mustard	1.0	Natural	0.5 %	3	See Table 4-12	3
Cell 1	White Mustard	1.0	Natural	1 %	3	See Table 4-12	3
						Total	18
Cell 7	Corn	1.0	5.5	0% (Control)	3	See Table 4-12	3
Cell 7	Corn	1.0	5.5	0.5 %	3	See Table 4-12	3
Cell 7	Corn	1.0	5.5	1 %	3	See Table 4-12	3
Cell 7	White Mustard	1.0	Natural	0% (Control)	3	See Table 4-12	3
Cell 7	White Mustard	1.0	Natural	0.5 %	3	See Table 4-12	3
Cell 7	White Mustard	1.0	Natural	1 %	3	See Table 4-12	3
						Total	18
						Grand Total	36

(1) Aerial plant samples taken during harvest.

Table 4-12

Chemical Analyses for the Foliar Application Study

Sample Type	Minimum Sample Size[1]	Parameter Measured
Plant (aerial)	7 grams	Total Metals (Pb, Ni, Zn)[2]
		Total P
Soil	17 grams	Plant-available Pb
		pH

(1) Every tenth sample contained twice the usual amount of sample and was submitted for use in the QA/QC program.

(2) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and is used to distinguish it from metals measured following a leaching process.

To conduct the study, plants were grown from seed in 5-inch diameter 8-inch deep plastic pots containing 2 kg of soil each. Midway through the plant growth period, phosphate was foliarly applied (i.e., applied to the plant leaves) using a fine mist sprayer. The amount of phosphate applied to each plant species was determined from literature values.[Ref.15] Only one phosphate application was made. When the crops reached full vegetative biomass, soil amendment treatments were applied to the pots, as indicated (Table 4-11). The plants were harvested, dried, weighed for biomass determination, ground, and analyzed for total metals (Pb, Ni, and Zn). Soil samples were analyzed for pH and plant-available lead.

4.5.3 Soil Leaching Study

Upon completing the Plant Screening and Foliar Application studies, the Soil Leaching Study was begun. During this study, the best plant species, chelate levels, and pH levels from the Plant Screening Study were used to examine:

- The movement of lead and EDTA through the soil column.
- Whether chelate application would induce leaching of solubilized lead.
- The potential impact of lead and residual EDTA on subsequent plant germination and growth.

The experimental procedures for this study were essentially the same as for the Foliar Application Study. The study was conducted using the parameters selected as optimal in the plant screening and foliar application studies. Treatment parameters included:

- Two soil types (soils from Cells 1 and 7)
- Two plant species (corn and white mustard)
- A 1.0 molar ratio of EDTA-to-soil lead
- Two soil pH (pH 5.5 for corn; natural pH for white mustard and all controls)
- No foliar application
- Two replicates of each variable (soil type, plant species, and soil pH) - the controls were not replicated

Details of the experimental design for the first growth period are provided in Table 4-13 and experimental design details for the second growth period are provided in Table 4-14. A listing of the chemical analyses performed is provided in Table 4-15.

The study was designed to incorporate information over two growing periods: one ten-week period in which chelate would be added to soil at full biomass (approximately week eight) and a subsequent ten-week period in which crops would be replanted in the soil and the impact of residual chelates would be tracked. Metal analyses in this study were limited to three metals (lead, nickel, and zinc).

To conduct the first growing test, the crops were grown from seed in soil columns measuring 6 inches in diameter by 30 inches in length. Each column contained 16 to 17 kg of soil. After the crops reached full vegetative biomass, and before amendment addition, the soil in each column was sampled at depths of 0"-6", 6"-12", 12"-18", and 18"-30" using a core sampler. A section of PVC pipe was inserted into the void where the soil core was removed to prevent short-circuiting of the amendment down the soil column (this was done throughout the study). The soil samples were analyzed (Table 4-15) for pH and total metals (Pb, Ni, and Zn) by ICP. The soil samples were further analyzed using a sequential extraction procedure, consisting of progressively stronger soil extractants (Appendix C-18), to determine the form of metal present. Plant root samples were also obtained with the core sampler. The root samples were analyzed for total metals (Pb, Ni, and Zn) by ICP.

After sampling the soil, the crops were treated with the appropriate soil amendments (Table 4-13). Approximately 2 to 4 days later, the crops were harvested and the soil was again sampled at depths of 0"-6", 6"-12", 12"-18", and 18"-30" using a core sampler. The soil samples were analyzed for:

- Soil pH
- Total metals (Pb, Ni, and Zn) by ICP analysis
- Total metals (Pb, Ni, and Zn) by sequential extraction followed by ICP analysis
- Plant-available lead
- Water-soluble EDTA

Table 4-13

Experimental Design Details for the 1st Growth Period of the Soil Leaching Study

Soil Source	Crop	Ratio of EDTA-to-Lead in Soil (Mole EDTA/Mole Pb)	Soil pH	Number of Replicates & Soil Depths	Chemical Analyses	Number of Soil Samples[1]	Number of Leachate Samples[2]	Number of Plant Samples[3]
Cell 1	Corn	1.0	5.5	2 reps 4 depths	See Table 4-15	2 reps X 4 depths X 2 sample times = 16	18 samples X 2 reps = 36 total	2 reps X 2 samples = 4 total
Cell 1	White Mustard	1.0	Natural	2 reps 4 depths	See Table 4-15	16	36	4
Cell 1	Corn (control)	None	Natural	1 rep 4 depths	See Table 4-15	1 reps X 4 depths X 2 sample times = 8	18	2
Cell 1	White Mustard (control)	None	Natural	1 reps 4 depths	See Table 4-15	8	18	2
					Total	48	108	12
Cell 7	Corn	1.0	5.5	2 reps 4 depths	See Table 4-15	2 reps X 4 depths X 2 sample times = 16	18 samples X 2 reps = 36 total	2 reps X 2 samples = 4 total
Cell 7	White Mustard	1.0	Natural	2 reps 4 depths	See Table 4-15	16	36	4
Cell 7	Corn (control)	None	Natural	1 rep 4 depths	See Table 4-15	1 reps X 4 depths X 2 sample times = 8	18	2
Cell 7	White Mustard (control)	None	Natural	1 reps 4 depths	See Table 4-15	8	18	2
					Total	48	108	12
					Grand Total	96	216	24

(1) Soil taken both pre- and post-harvest.
(2) Leachate samples were to be obtained from each replicate once every two weeks prior to adding soil amendment (4 times/crop) and every day afterward.
(3) Both aerial and root samples are taken during harvest.

Table 4-14

Experimental Design Details for the 2nd Growing Period of the Soil Leaching Study

Soil Source	Crop	Ratio of EDTA-to-Lead in Soil (Mole EDTA/Mole Pb)	Soil pH	Number of Replicates & Soil Depths	Chemical Analyses	Number of Soil Samples[1]	Number of Leachate Samples[2]	Number of Plant Samples[3]
Cell 1	Corn	1.0	5.5	2 reps 4 depths	See Table 4-15	2 reps X 4 depths X 1 sample time = 8	10 samples X 2 reps = 20 total	2 reps X 2 samples = 4 total
Cell 1	White Mustard	1.0	Natural	2 reps 4 depths	See Table 4-15	8	20	4
Cell 1	Corn (control)	None	Natural	1 rep 4 depths	See Table 4-15	1 rep X 4 depths X 1 sample time = 4	10 samples X 1 reps = 10 total	1 reps X 2 samples = 2 total
Cell 1	White Mustard (control)	None	Natural	1 reps 4 depths	See Table 4-15	4	10	2
					Total	24	60	12
Cell 7	Corn	1.0	5.5	2 reps 4 depths	See Table 4-15	2 reps X 4 depths X 1 sample time = 8	10 samples X 2 reps = 20 total	2 reps X 2 samples = 4 total
Cell 7	White Mustard	1.0	Natural	2 reps 4 depths	See Table 4-15	8	20	4
Cell 7	Corn (control)	None	Natural	1 rep 4 depths	See Table 4-15	1 rep X 4 depths X 1 sample time = 4	10 samples X 1 reps = 10 total	1 reps X 2 samples = 2 total
Cell 7	White Mustard (control)	None	Natural	1 reps 4 depths	See Table 4-15	4	10	2
					Total	24	60	12
					Grand Total	48	120	24

(1) Soil taken both pre- and post-harvest.
(2) Leachate samples were to be obtained from each replicate every week (10 times/crop).
(3) Both aerial and root samples are taken during harvest.

Table 4-15

Chemical Analyses for the Soil Leaching Study

Sample Type	Minimum Sample Size[1]	Preservative Added	Growing Period	Sample Time	Parameter Measured
Soil	45 grams	None	1st Growing Period	Before Soil Amendment Application	pH Total Metals (Pb, Ni, Zn)[2] Total Metals (Pb, Ni, Zn) by Sequential Analysis
			2nd Growing Period	Before Soil Amendment Application	pH Total Metals (Pb, Ni, Zn)[2] Total Metals (Pb, Ni, Zn) by Sequential Analysis Chelate (water-soluble EDTA)
			1st and 2nd Growing Periods	After Crop Harvest	pH Total Metals (Pb, Ni, Zn)[2] Total Metals (Pb, Ni, Zn) by Sequential Analysis Plant-available Pb Chelate (water-soluble EDTA)
Leachate	215 ml	Filtered[3] then Nitric Acid added. (until pH <2)	1st and 2nd Growing Periods	See Tables 4-13 and 4-14	Total Dissolved Metals (Pb, Ni, Zn)
Plants (Root)	10 grams[2]	None	1st and 2nd Growing Periods	Before Amendment Application and After Crop Harvest	Total Metals (Pb, Ni, Zn)[2]
Plants (Aerial)				After Crop Harvest	Total Metals (Pb, Ni, Zn)[2] Pb by Scanning Electron Microscope

(1) Every tenth sample will contain twice the usual amount of sample and was submitted for use in the QA/QC program.

(2) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and is used to distinguish it from metals measured following a leaching process.

(3) Filtered through Whatman #2 or equivalent.

Plant root and aerial shoots samples were also collected at this time. The plant samples were harvested, dried, weighed for biomass determination, ground, and analyzed for:

- Total metals (Pb, Ni, and Zn) by ICP
- Lead by electron scanning microscope (SEM)

An Electro Scan 3 environmental electron scanning microscope equipped with a PGA Omega energy dispersive X-ray detector (EDX) was used to detect the location of lead and other metals in the plant. This analysis was done to determine the sites of lead accumulation in the aerial parts of the plant, which in turn may indicate the movement and deposition of lead in the plant. Identifying where the lead is located in the plant may also be a means of determining the appropriate harvesting techniques to minimize the possibility of dispersing contaminated shoot tissues.

Each column was fitted with a leachate collection system consisting of a central drain leading to a plastic sampling bottle located at the bottom of the column. However, leachate collection was impaired due to the effect on soil percolation of sodium in the tri-sodium salt of EDTA applied to the soil, and representative leachate samples could not be collected. In addition, reduced germination and stunting of surviving plants of both corn and white mustard occurred in replanted columns that had received soil amendments. Results of germination and growth experiments indicated that the sodium in the tri-sodium salt of EDTA was the most likely cause of reduced germination in plants of a subsequent crop after initial EDTA additions.

For the second growing period (i.e. the replanting period), the columns used as controls in the first growth period were replanted with corn and white mustard, with the experimental procedure the same as for the first growth period. Leachate was collected before soil amendments were added, but restricted water percolation again prevented collection of leachates after the addition of the soil amendments. This also caused pooling of water on the soil surface which prevented post-chelate soil sampling.

To determine why the crops were failing, TVA conducted germination and growth tests. These test results suggested that the problem was a combination of:

- Excess sodium which inhibited seed germination
- Excess EDTA which may be phytotoxic

The most likely sodium source was the EDTA which was introduced as a tri-sodium salt of EDTA.

The reaction of sodium with soil clay micelles caused a flocculation of soil particles and loss of pore space for water infiltration. This "puddling" of the soil, as it is known, greatly restricted water movement from the soil surface downward to the bottom of the column, which precluded collection of leachate samples. Some downward movement of water eventually occurred, as indicated by a reduction in the amount of water standing on the soil surface. This likely was not due to evaporation loss since the soil surface was about 4 inches below the top of the column, and the relatively narrow diameter of the columns minimized air exposure to air currents. The soil was subsequently sampled at incremental depths to determine if movement of metals or chelate may have occurred. However, representative leachate samples could not be collected.

In an attempt to overcome this problem, a Lysimeter Study was added to the project. To minimize the effects of sodium, the Lysimeter Study was conducted with tri-potassium EDTA.

4.5.4 Lysimeter Study

The Lysimeter Study was an attempt to better determine the amount and extent of lead and EDTA movement downward though the soil, while allowing for observation of actual solution migration through the soil. The slow infiltration rate of the natural soil, which was complicated further by the sodium in the added EDTA, did not allow this in the Soil Leaching Study. Porous cup soil water samplers (suction lysimeters) were inserted through the side of each column at various depths to sample water directly from the soil, rather than depending on leaching. In an attempt to improve water percolation through the soil by eliminating the large amount of sodium added in the previous Soil Leaching Study, tri-potassium EDTA was used in this study. Details of the experimental design are given in Table 4-16, and a listing of the chemical analyses performed is provided in Table 4-17.

Table 4-16

Experimental Design Details for the Lysimeter Study of the Soil Leaching Study

Soil Source	Crop	Ratio of EDTA to Lead in Soil (Mole EDTA/Mole Pb)	Soil pH	Number of Replicates & Soil Depths	Chemical Analyses	Number of Soil Samples[1]	Number of Leachate Samples[2]	Number of Plant Samples[3]
Cell 7	White Mustard	1.0	Natural	2 reps 4 depths	See Table 4-17	2 reps X 4 depths X 2 sample times = 16	15 samples X 2 reps = 30 total	2 reps x 2 samples = 4
					Total	16	30	4

(1) Soil taken both pre- and post-harvest.
(2) Leachate samples obtained prior to soil amendment addition and every day there after until harvest
(3) Both aerial and root samples are taken during harvest.

Table 4-17

Chemical Analyses for the Lysimeter Study

Sample Type	Minimum Sample Size[1]	Preservative Added	Sample Time	Parameter Measured
Soil	45 grams	None	Before Soil Amendment Application	pH Total Metals (Pb, Ni, Zn)[2]
			After Crop Harvest	pH Total Metals (Pb, Ni, Zn)[2]
Leachate	215 ml	Filtered[3] then Nitric Acid added. (Until pH<2)		Total Dissolved Metals (Pb, Ni, Zn)
Plants (Root)	10 grams[2]	None	Before Amendment Application and After Crop Harvest	Total Metals (Pb, Ni, Zn)[2]
Plants (Ariel)	10 grams[2]	None	Before Amendment Application and After Crop Harvest	Total Metals (Pb, Ni, Zn)[2]

(1) Every tenth sample will contain twice the usual amount of sample and was submitted for use in the QA/QC program.

(2) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and is used to distinguish it from metals measured following a leaching process.

(3) Filtered through Whatman #2 or equivalent.

The Lysimeter Study experimental design was very similar to the design created for the Soil Leaching Study, except:

- Only Cell 7 soil was used (all the Cell 1 soil was used in previous studies)
- The study was conducted over one growing period due to the limited time remaining for study.
- The white mustard treatment was investigated because corn would not grow in the greenhouse at the time the study was conducted
- No controls were used due to an insufficient amount of soil

The study obtained information over a ten-week growing period, with tri-potassium EDTA being added at approximately week eight when the plants reached full biomass. The amendment treatment consisted of a 1.0 molar ratio of EDTA/soil-borne lead at the natural soil pH.

To conduct the Lysimeter Study, two 6-inch-diameter, 30-inch long transparent Lucite columns were fitted with four lysimeters. Each column contained approximately 17 kg of soil from Cell 7. The lysimeters were placed at depths of 6, 12, 18, and 24 inches. Any leachate moving through the soil column was to be intercepted as it moved through the soil column. Transparent Lucite columns were used to visually observe leachate movement.

The columns were planted with white mustard. After the plants had reached full biomass, an amount of EDTA was added in a sufficient volume of water to give an EDTA-to-soil molar ratio of 1.0 in the top 24 inches of the column, and to bring the top 24 inches to field capacity.

Leachate was to be collected one time at all depths before EDTA addition and daily at all depths after EDTA addition (Table 4-17). However, the low hydraulic conductivity of these heavy textured soils apparently severely restricts water movement through the soil. During the normal growing period, the columns received only an amount of water sufficient to meet the needs of the growing plants, and no leaching occurred. After the plants had died and were harvested, an attempt was made to induce leachate collection

by adding large volumes of water to the soil. However, even under these circumstances, only 10% of the water infiltrated into the soil after 24 hours.

Soil and root samples were also taken prior to adding EDTA to the soil. The soil in each column was sampled at depths of 0"-6", 6"-12", 12"-18", and 18"-30" using a core sampler. The soil samples were analyzed (Table 4-17) for pH and total metals (Pb, Ni, and Zn) by ICP. Plant shoot and root samples were also obtained. The plant parts were harvested, dried, ground, and analyzed for total metals (Pb, Ni, and Zn) by ICP.

Approximately two days after adding the EDTA, the white mustard crop was harvested and the soil was again sampled at depths of 0"-6", 6"-12", 12"-18", and 18"-30" using a core sampler. The soil samples were analyzed for total metals (Pb, Ni, and Zn) by ICP.

Plant root and aerial shoot samples were also collected at this time. The plant parts were harvested, dried, weighed for biomass determination, ground, and analyzed for total metals (Pb, Ni, and Zn) by ICP.

4.5.5 <u>Chelate Application Timing Study</u>

The Chelate Application Timing Study was designed to refine the timing of chelate application for white mustard. The premise for this study was that the plant capacity to take up lead should be at a maximum when plant water uptake is at a maximum. The most rapid rate of water uptake by white mustard begins at bolting (rapid stem elongation immediately prior to flowering) and continues through flowering. The study was necessary to determine the time of chelate application for maximum lead uptake by the plant.

During this study, chelate was added to three replicate pots during bolting, but before flowering, and to a second set of pots during bolting after flowering had begun. Sufficient chelate was added to give an EDTA-to-soil lead ratio of 1.0. Each pot contained 1 kg of soil from Cell 7. Soil from Cell 1 was not used in this study because

the available supply had been depleted by previous studies. The soil pH was not adjusted. The aerial portions of the plant were harvested after senescence and analyzed for total lead.

Details of the experimental design are provided in Table 4-18 and a listing of the chemical analyses performed is provided in Table 4-19.

4.5.6 Harvest Timing Study

The Harvest Timing Study was designed to the determine the time required after chelate addition for maximum lead accumulation by the plant before senescence. The length of time required for maximum lead accumulation has a direct bearing on harvesting efficiency. If plants could be harvested within a short time after chelate addition, before the leaves dried out due to plant death, shattering and wind dispersion of dried leaves could be minimized.

To conduct this study, fifteen plastic pots containing 1 kg of soil from Cell 7 were planted with white mustard. Soil from Cell 1 was not used in this study because the available supply had been consumed in previous studies. Chelate was added at bolting to give an EDTA-to-soil lead ratio of 1.0. The soil pH was not adjusted. The aerial portion of plants from three replicate pots was harvested at 24, 48, 72, 96, and 108 hours after chelate addition, and the plant tissues were analyzed for total lead.

Details of the experimental design are provided in Table 4-20, and a listing of the chemical analyses performed is provided in Table 4-21.

4.6 Analytical Methods

The analytical methods used to analyze soil, plant, and leachate samples are outlined in Tables 4-22, 4-23, 4-24 and respectively.

Table 4-18

Experimental Design Details for the Chelate Application Timing Study

Soil Source	Crop	Ratio of EDTA-to-Lead in Soil (Mole EDTA/Mole Pb)	Soil pH	Chelate Application Time	Number of Replicates	Chemical Analyses	Number of Plant Samples
Cell 7	White Mustard	1.0	Natural	Before flowering	3	See Table 4-19	3
Cell 7	White Mustard	1.0	Natural	During flowering	3	See Table 4-19	3
						Total	6

Table 4-19

Chemical Analyses for the Chelate Application Timing Study

Sample Type	Minimum Sample Size[1]	Parameter Measured
Plant (aerial)	7 grams	Total Metals (Pb)[2]

(1) Every tenth sample contained twice the usual amount of sample and was submitted for use in the QA/QC program.

(2) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and is used to distinguish it from metals measured following a leaching process.

Table 4-20

Experimental Design Details for the Harvest Timing Study

Soil Source	Crop	Ratio of EDTA-to-Lead in Soil (Mole EDTA/Mole Pb)	Soil pH	Harvest Time	Number of Replicates	Chemical Analyses	Number of Plant Samples
Cell 7	White Mustard	1.0	Natural	24, 38, 72, 96, and 108 hours	3	See Table 4-21	5 harvest times X 3 reps = 15
						Total	15

Table 4-21

Chemical Analyses for the Harvest Timing Study

Sample Type	Minimum Sample Size[1]	Parameter Measured
Plant (aerial)	7 grams	Total Metals (Pb)[2]

(1) Every tenth sample contained twice the usual amount of sample and was submitted for use in the QA/QC program.

(2) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and is used to distinguish it from metals measured following a leaching process.

Table 4-22

Soil Analyses: Outline of Parameters Analyzed and Method

Parameter Measured	Extraction or Preparation Method	Analytical Method
pH	N/A	ASA 12-2.6
Buffer Curves	N/A	Appendix C-21
Cation Exchange Capacity (CEC)	N/A	ASA 9-3.1/9-4.2
Total Organic Carbon (TOC)	N/A	ASA 29-3.5.2
Total Kjeldahl Nitrogen (TKN)	N/A	AP-0064
Extractable P	ASA 24-5.2	6010B
Extractable K	ASA 9-3.1	6010B
Exchangeable Ca	ASA 9-3.1	6010B
Exchangeable Mg	ASA 9-3.1	6010B
Exchangeable Al	ASA 9-4.2	6010B
DTPA-Extractable Fe	ASA 17-4.3	6010B
DTPA-Extractable Mn	ASA 17-4.3	6010B
Total Metals (Cd, Cu, Mo, Ni, Zn, Cr, Pb)[1]	3050B	6010B
Total Metals (Hg)[1]	7471A	7471A
Total Metals (Se)[1]	7740	7740
EDTA-Soluble Pb	ASA 21-5	6010B
Plant-Available Pb[2]	ASA 21-5	6010B
Total Metals by Sequential Analysis	AP-0054[3]	6010B
Chelates	AP-0057	AP-0047
Soil Moisture	N/A	ASA 21-2.2.2
Moisture Release Curves (Field Capacity)	N/A	ASA 8-2.3

1) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and is used to distinguish it from metals measured following a leaching process.

2) Plant-available lead and water-soluble lead are synonymous terms.

3) Sequential extraction of metals in soil was performed using the method outlined in: Tessier, A., P.G.C. Campbell and M. Bisson. 1979.[ref. 16] Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51:844-850. (See Appendix C-18.)

Table 4-23

Plant Analyses: Outline of Parameters Analyzed and Method

Parameter Measured	Extraction or Preparation Method	Analytical Method
Total Metals (Ni, Pb, Zn)[1]	3050B	6010B
Pb sequestration	---	SEM-EDX[2]
Total P	3050B	6010B

1) The term "Total Metals" for any element refers to an analysis following an acid digestion of the sample and is used to distinguish it from metals measured following a leaching process.

2) Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray Detector.

Table 4-24

Leachate Analyses: Outline of Parameters Analyzed and Method

Parameter Measured	Preparation Method	Analytical Method
Total Dissolved Metals (Pb, Ni, Zn)	3005A	6010B

4.7 Data Analysis

All data reported in this document were the analytical means of at least duplicate treatment replications. To detect differences in outcomes due to treatment effects, appropriate portions of the data were analyzed using the Least Significant Difference Test (LSD). The LSD test is a statistical procedure for making pair comparisons of treatment means and is commonly used in agricultural research. The procedure provides for a single LSD value, at a prescribed level of significance, which serves as the boundary between significant and non-significant differences between any pair of treatment means. That is, two treatments are declared significantly different at a prescribed level of significance if the difference between the means exceeds the computed absolute value of the LSD value; otherwise they are not significantly different. Thus, the test indicates if there is a difference in results due to treatments.

The LSD is calculated at a given level of significance by taking the difference between any two treatment means, then taking the standard error of the mean difference. This standard error is multiplied by a "t" value which has assigned to it a level of significance and a certain number of degrees of freedom (d.f.), which in this case was four. The "t" value is taken from standard statistical tables.

The value for the mean difference computed as described above is then compared to the calculated LSD value. If the absolute value of the difference between treatment means is greater than the absolute value of the LSD, the means are then declared to be significantly different. Otherwise the difference between the two means is not significantly different.

4.8 Laboratory Equipment

The equipment used for analyzing samples is outlined in Table 4-25.

Table 4-25

Laboratory Equipment Used

Laboratory Data	Equipment
Chelates	Varian HPLC
DTPA-Extractable Fe and Mn	Perkin Elmer or Thermo Jarrel Ash ICP
Extractable P	Perkin Elmer or Thermo Jarrel Ash ICP
Exchangeable K, Ca, Mg, and Al	Perkin Elmer or Thermo Jarrel Ash ICP
TKN	Lachat Quick Chem 8000 or Technicon AutoAnalyzer II
Total Organic Carbon (TOC)	Manual Titration
Total Metals (Pb, Cd, Cu, Mo, Ni, Zn, Cr)	Perkin Elmer or Thermo Jarrel Ash ICP
Total Metals (Hg)	Cold Vapor Atomic Absorption (AA) or Perkin Elmer or Thermo Jarrel Ash ICP
Total Metals (Se)	Graphite Furnace Atomic Absorption or Perkin Elmer or Thermo Jarrel Ash ICP
Total Lead (Pb)	Perkin Elmer or Thermo Jarrel Ash ICP
EDTA-Soluble lead (Pb)	Perkin Elmer or Thermo Jarrel Ash ICP
Plant-Available lead (Pb)	Perkin Elmer or Thermo Jarrel Ash ICP
Total Metals by Sequential Analysis	Perkin Elmer or Thermo Jarrel Ash ICP
Total Pb by Sequential Analysis	Perkin Elmer or Thermo Jarrel Ash ICP
pH	Orion meter or equivalent

SECTION 5.0
RESULTS

5.1 Soil Characterization

The two soils obtained from SFAAP consisted of a Kennebec silty clay of near neutral pH from Cell 1 and Kennebec silt loam from Cell 7. A partial characterization of these soils is provided in Table 5-1. Generally, these were fertile soils which could supply adequate levels of most macro- and micro-nutrients required for good plant growth. However, the soil from Cell 1 was low in phosphorus (20 mg P/kg soil, Table 5-1) according to standard soil test recommendations. Lead concentrations averaged 2,530 mg/kg in Cell 1 soil and 3,445 in Cell 7 soil. The soils natural plant-available lead concentrations were very low, which indicates that plants in these soils would not take up large quantities of lead under normal growing conditions. Although the soils were analyzed for heavy metals, only zinc, nickel, and lead were detected in significant concentrations, whereas the other metals (cadmium, chromium, copper, mercury, molybdenum, and selenium) were below detection limits in the majority of samples (Table 5-1). Therefore, with the exception of the Chelate Screening Study, metal analyses for the project were limited to these three metals. Testing indicated that the field capacity of both soils was 32% moisture by weight. All of the studies were conducted with the soil at field capacity.

5.2 Preliminary Laboratory Studies

5.2.1 Chelate Screening Study

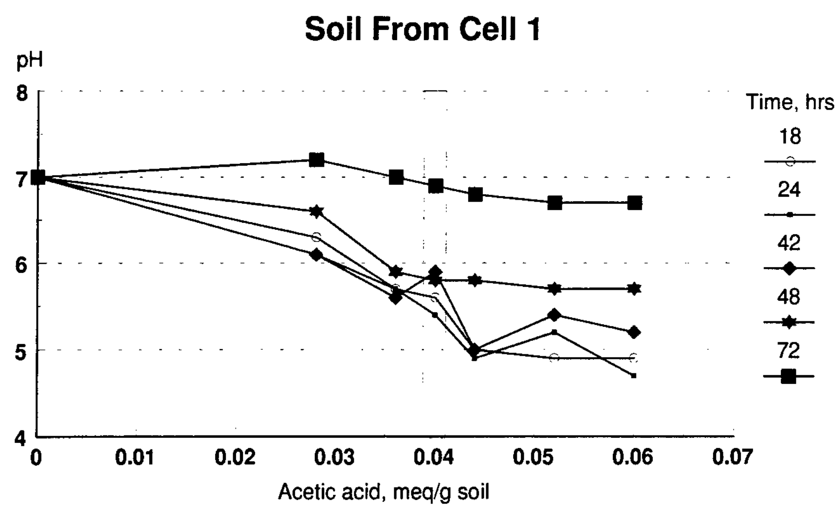
The efficiency of different chelates was evaluated during the Chelate Screening Study. To accomplish this, varying chelate concentrations were used to solubilize ionic metals at different soil pH levels. Prior to initiation of the Chelate Screening Study, buffer curves (Figure 5-1) were determined by adding solutions of acetic acid at concentrations ranging from 0.028 millequivalents per gram of soil (meq/g) to 0.06 meq/g to plastic pots containing 500g of each soil. The soil pH was determined after the soils had equilibrated for periods ranging from 18 hours to 72 hours. The optimum concentration of acetic acid was the amount which reduced soil pH to 5.5 after 18-24 hours.

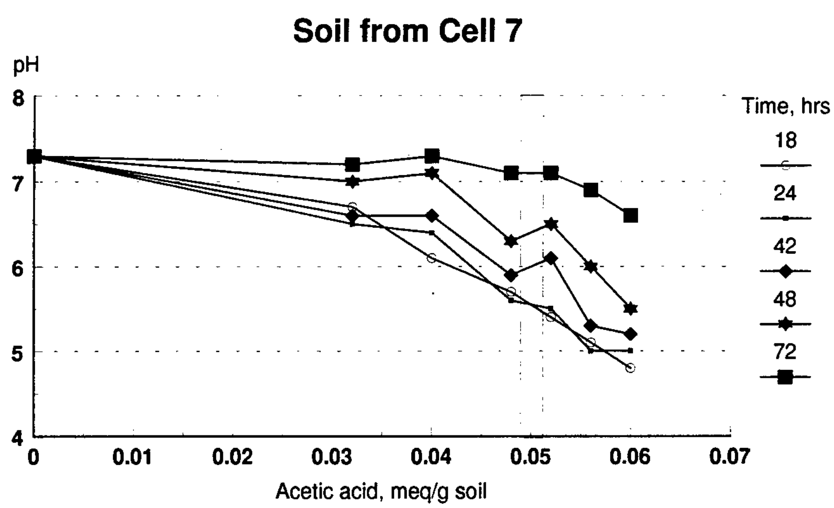
Table 5-1

Soil Characterization: Partial Characterization of Contaminated Soil

Characteristic	Cell 1 Soil [1]	Cell 7 Soil [1]
Texture	silty clay	loam
pH	7.0	7.3
CEC, cmol/kg	18.9	15.7
Field capacity, %	32	32
Organic carbon, %	1.4	1.8
TKN, %	0.16	0.28
Total Pb, mg/kg	2,530 range: 1,720-3,200 [2]	3,445 range: 362-3,660 [2]
Plant-Available Pb, mg/kg	32	47
EDTA-Soluble Pb, mg/kg	1,898	2,837
Exchangeable Al, mg/kg	0.2	0.3
Exchangeable Ca, mg/kg	2,446	2,542
Exchangeable Mg, mg/kg	157	437
Extractable P, mg/kg	20	44
Exchangeable K, mg/kg	145	196
DTPA-Extractable Fe, mg/kg	63	72
DTPA-Extractable Mn, mg/kg	33	11
Total Cd, mg/kg	3	3
" Cr "	24	23
" Cu "	29	31
" Hg "	<0.3	<0.3
" Mo "	<0.5	<0.5
" Ni "	21	28
" Se "	<1.2	<1.2
" Zn "	112	269

1) Mean from 12 samples collected from bulk piles of each soil.
2) Mean of 72 samples across the entire field.





Note: the dotted boxes indicate the actual concentrations of acetic acid used to adjust the soil pH in subsequent studies.

Figure 5-1

Acetic Acid Buffer Curves

Of the chelates tested (EDTA, EGTA, and CDTA), EDTA was the most effective. The EDTA solubilized an average of 60 percent of the soil total lead when applied at a rate of 15 mmole/kg. These results were obtained in both soils, both at the soil natural pH and when the soils were acidified to a pH of 5.5 (Tables 5-2 and 5-3 and Figure 5-2). CDTA was almost as effective as EDTA, but is more expensive than EDTA.

5.2.2 Chelate Application Study

Application of EDTA to small soil columns was performed to determine movement and persistence of EDTA in soil, the effect of EDTA on lead leaching through the soil profile, and the optimum solution volume to be applied.

Water-soluble EDTA moved down the soil columns when the EDTA was applied as a solution containing enough water to bring the soil to 1.0 or 1.5 times field capacity (Figure 5-3). The water-soluble EDTA appeared to move down to the 6"-12" and 12"-18" portions of the columns containing soil from Cell 1. Little movement into the 18"-24" section of the columns was observed, except when the solution was applied at 1.5 times field capacity. This indicates that excess water (1.5 times field capacity) enhanced movement of EDTA to lower soil depths in Cell 1. Little downward movement in Cell 7 soil was observed. To fully saturate the root zone in a soil like that from Cell 7, it may be necessary to increase the amount of water used to apply the chelate. These test results suggest that chelate movement out of Cell 1 root zone (top two feet) can be minimized if the volume of EDTA solution added brings only the root zone to field capacity.

Water-soluble EDTA remained in the soils four weeks after the chelate was applied (Figure 5-3). Generally, the water-soluble EDTA concentrations remained constant with time indicating that the EDTA was not degrading. A chelate mass balance was not conducted since the amount of solution added did not promote leaching.

The total lead profiles for the soil columns were similar to the profiles for water-soluble EDTA. Higher lead concentrations were seen in the 18"-24" sections of the columns when excess water was applied to bring the columns to 1.5 times field capacity as compared to

Table 5-2

Chelate Screening Study: Effects of Chelate Type, Chelate Concentration, and Soil Acidification on the Extraction of Metals from Cell 1 Soil

Chelate	Chelate Concentration (mmoles/100g soil)	Acetic Acid, (meq/g soil)	Total Metals Extracted, mg					
			Pb	Cd	Cr	Cu	Ni	Zn
At the Soil's Natural pH								
EDTA	0.015	0	6.5	0.0	0.0	0.1	0.0	0.2
	0.15	0	24.8	0.0	0.0	0.1	0.0	0.4
	1.5	0	143	0.0	0.0	0.6	0.3	1.9
EGTA	0.015	0	6.0	0.0	0.0	0.2	0.0	0.2
	0.15	0	6.6	0.0	0.0	0.4	0.0	0.6
	1.5	0	14.9	0.0	0.0	0.6	0.1	1.2
CDTA	0.015	0	7.6	0.0	0.0	0.1	0.0	0.3
	0.15	0	24.0	0.0	0.0	0.2	0.0	0.7
	1.5	0	133	0.1	0.0	0.7	0.3	1.9
Control	Distilled Water	0	6.9	0.0	0.0	0.1	0.0	0.3
		$LSD_{0.05}$[1]	2.8	---	---	0.03	0.01	0.09
At a Soil pH of 5.5								
EDTA	0.015	0.05	1.4	0.0	0.0	0.0	0.0	0.0
	0.15	0.05	15.8	0.0	0.0	0.0	0.0	0.2
	1.5	0.05	139	0.0	0.0	0.4	0.4	1.8
EGTA	0.015	0.05	0.2	0.0	0.0	0.1	0.0	0.0
	0.15	0.05	1.3	0.0	0.0	0.5	0.0	0.5
	1.5	0.05	26.5	0.0	0.0	0.8	0.2	1.6
CDTA	0.015	0.05	1.7	0.0	0.0	0.1	0.0	0.1
	0.15	0.05	16.7	0.0	0.0	0.2	0.0	0.5
	1.5	0.05	113	0.1	0.0	0.8	0.3	1.9
Control	Acetic Acid	0.05	0.5	0.0	0.0	0.0	0.0	0.0
		$LSD_{0.05}$[1]	7.2	---	---	0.08	0.01	0.09

1) $LSD_{0.05}$ – Least significant difference at the 5% probability level.

Table 5-3

Chelate Screening Study: Effects of Chelate Type, Chelate Concentration, and Soil Acidification on the Extraction of Metals from Cell 7 Soil

Chelate	Chelate Concentration (mmoles/100g soil)	Acetic Acid, (meq/g soil)	Total Metals Extracted, mg					
			Pb	Cd	Cr	Cu	Ni	Zn
At the Soil's Natural pH								
EDTA	0.015	0	9.4	0.0	0.0	0.0	0.0	0.7
	0.15	0	33.5	0.0	0.0	0.1	0.0	1.3
	1.5	0	195	0.1	0.0	0.5	0.3	5.9
EGTA	0.015	0	7.9	0.0	0.0	0.1	0.0	0.8
	0.15	0	9.4	0.1	0.0	0.3	0.0	1.4
	1.5	0	34.3	0.1	0.0	0.5	0.1	3.1
CDTA	0.015	0	10.3	0.0	0.0	0.1	0.0	0.9
	0.15	0	31.5	0.0	0.0	0.1	0.0	2.1
	1.5	0	186.	0.1	0.0	0.7	0.3	6.5
Control	Distilled Water	0	7.7	0.0	0.0	0.1	0.0	0.6
		$LSD_{0.05}$[1]	4.9	---	---	0.03	0.01	0.03
At a Soil pH of 5.5								
EDTA	0.015	0.05	2.4	0.0	0.0	0.0	0.0	0.2
	0.15	0.05	14.9	0.0	0.0	0.0	0.0	0.4
	1.5	0.05	152	0.1	0.0	0.2	0.3	4.5
EGTA	0.015	0.05	0.1	0.0	0.0	0.1	0.0	0.2
	0.15	0.05	4.4	0.1	0.0	0.4	0.0	1.4
	1.5	0.05	60.7	0.1	0.0	0.8	0.2	5.0
CDTA	0.015	0.05	1.9	0.0	0.0	0.0	0.0	0.2
	0.15	0.05	9.4	0.0	0.0	0.0	0.0	0.8
	1.5	0.05	113	0.1	0.0	0.8	0.3	1.9
Control	Acetic Acid	0.05	0.0	0.0	0.0	0.0	0.0	0.1
		$LSD_{0.05}$[1]	7.2	---	---	0.05	0.02	0.03

1) $LSD_{0.05}$ – Least significant difference at the 5% probability level.

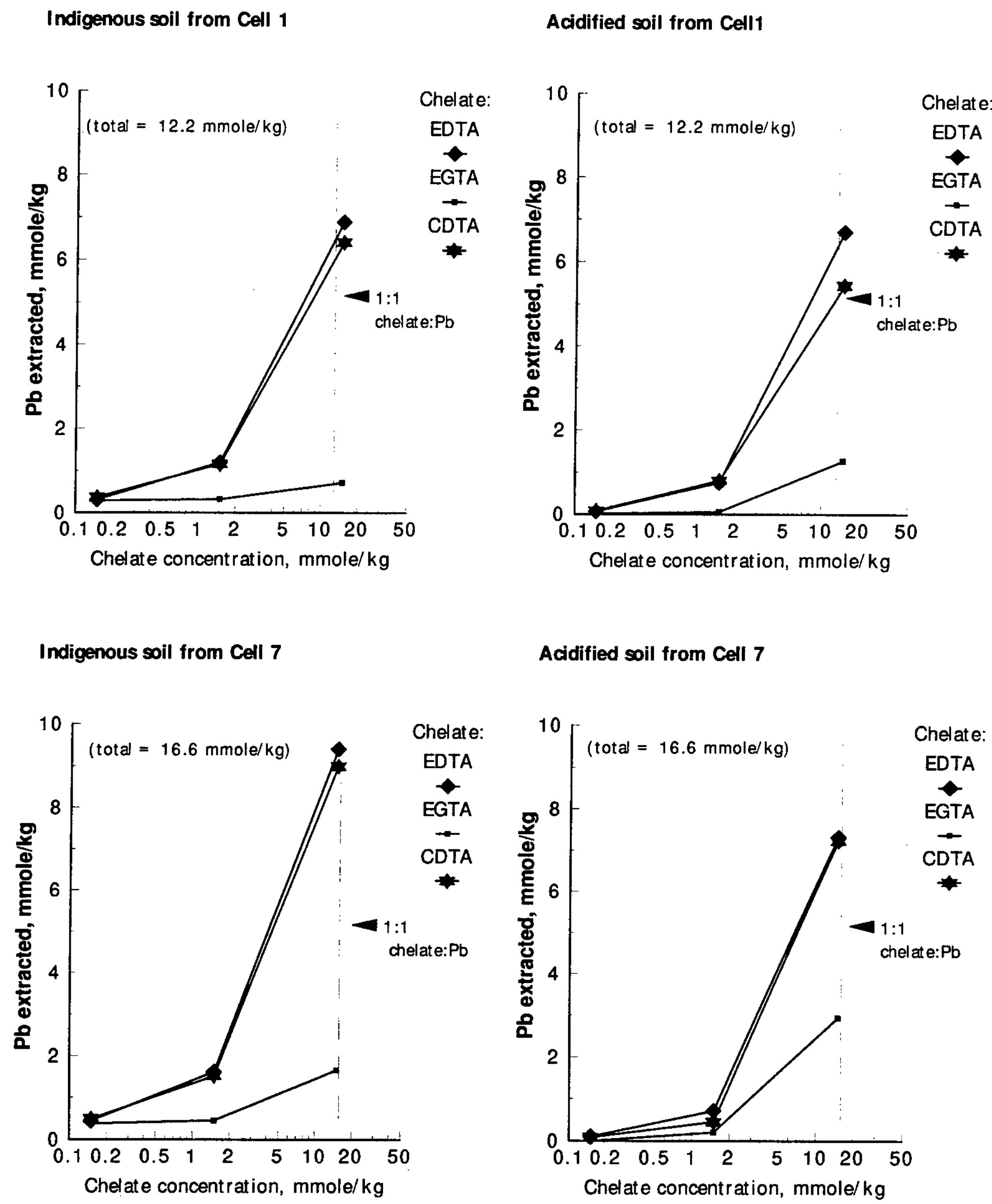


Figure 5-2

Chelate Screening Study

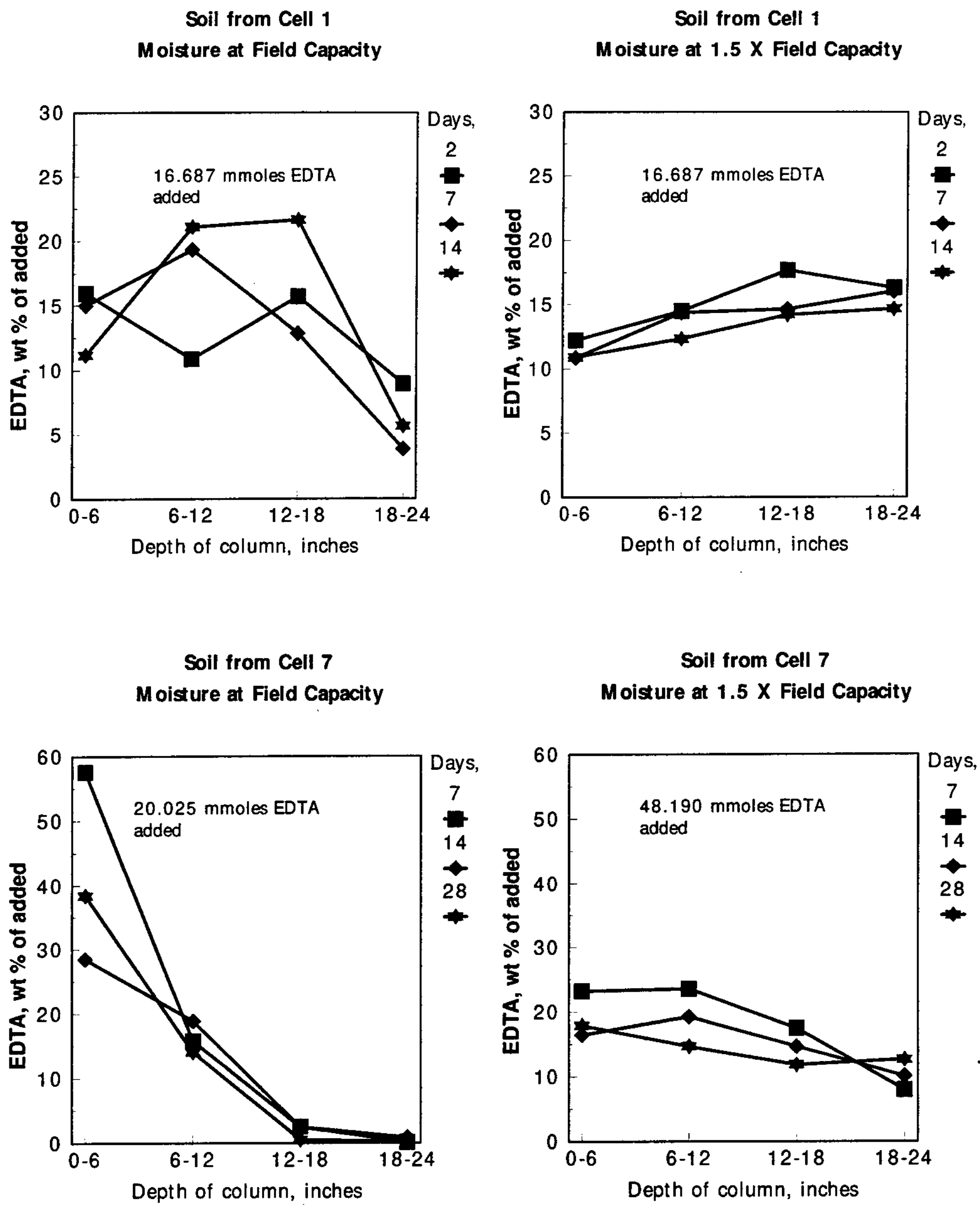


Figure 5-3

Chelate Application Study: Soluble EDTA Versus Soil Depth

columns at 1.0 times field capacity (Figure 5-4). Similar results were found in the analyses of plant-available lead (Figure 5-5). Very little plant-available lead was detected in the 18"-24" sections for columns that were at field capacity, with the majority of lead accumulating either in the 6"-12" or the 12"-18" sections. However, columns at 1.5 times field capacity showed the highest levels of plant-available lead in the 18"-24" sections. These results reinforce the premise that EDTA should not be applied in volumes of water which exceed the soil field capacity in the root zone.

5.3 Greenhouse Studies

5.3.1 Plant Screening Study

The Plant Screening Study was conducted to determine:

- The cool and warm season plant species most efficient at taking up lead from the soil
- The amount of EDTA to add to the soil
- The need for soil acidification to optimize lead removal

Corn (*Zea mays* L.) was the most efficient of the warm season crops (corn, sorghum sudan grass [*Sorghum sudanense* L.], and sunflower [*Helianthus annus* L.] at lead uptake. When the soils were left at the natural pH, lead uptake by corn was <100 ppm (Figure 5-6). However, corn did accumulate lead when the soil pH was decreased. In both soils, the optimum conditions for lead uptake occurred when the soil pH was adjusted to 5.5 and the EDTA-to-lead ratio was between 1.0 and 1.5 on a molar basis (Figure 5-6). An EDTA-to-lead ratio of 1.0 is recommended, since increasing the EDTA/lead ratio to 1.5 did not significantly increase lead uptake, but would increase the cost of field application.

The average lead concentration found in the harvested corn was 0.85%. This level is consistent with levels found by other investigators. Huang (1997) reported lead concentrations in corn up to 0.25% in a soil with a lead concentration similar to that found in Cell 1 soil (2,500 mg lead/kg soil). A related experiment [Ref. 17] produced lead concentrations up to 1.06% in corn. However, the corn seedlings were only 17 days old. These results do not extrapolate

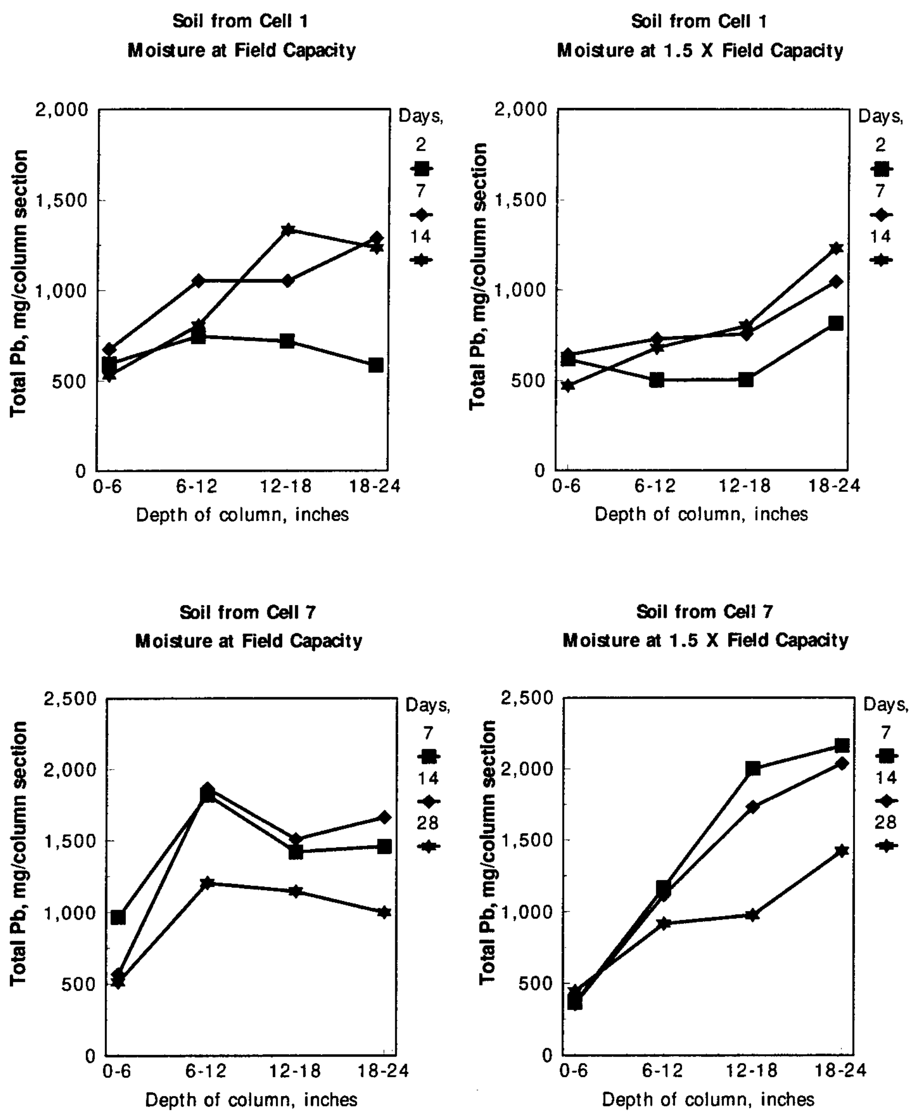


Figure 5-4

Chelate Application Study: Total Lead Versus Soil Depth

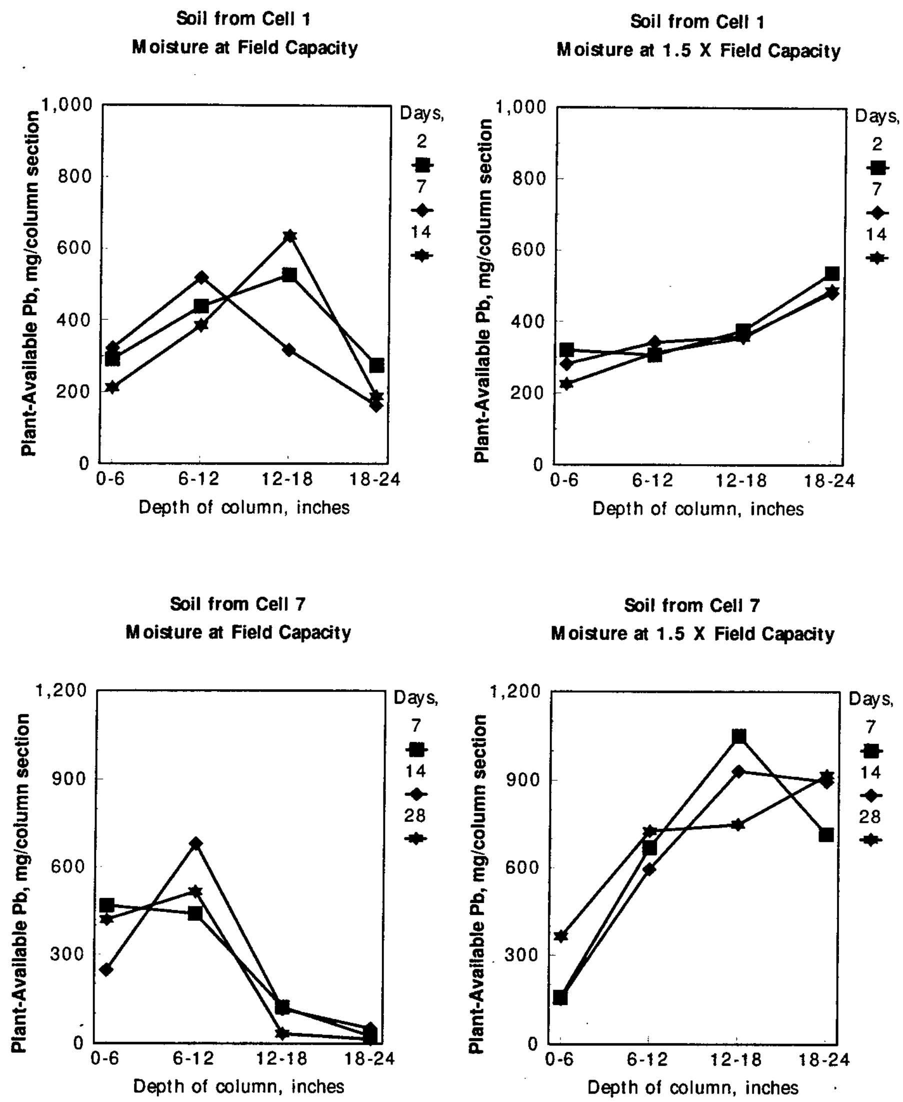


Figure 5-5

Chelate Application Study: Plant-Available Lead Versus Soil Depth

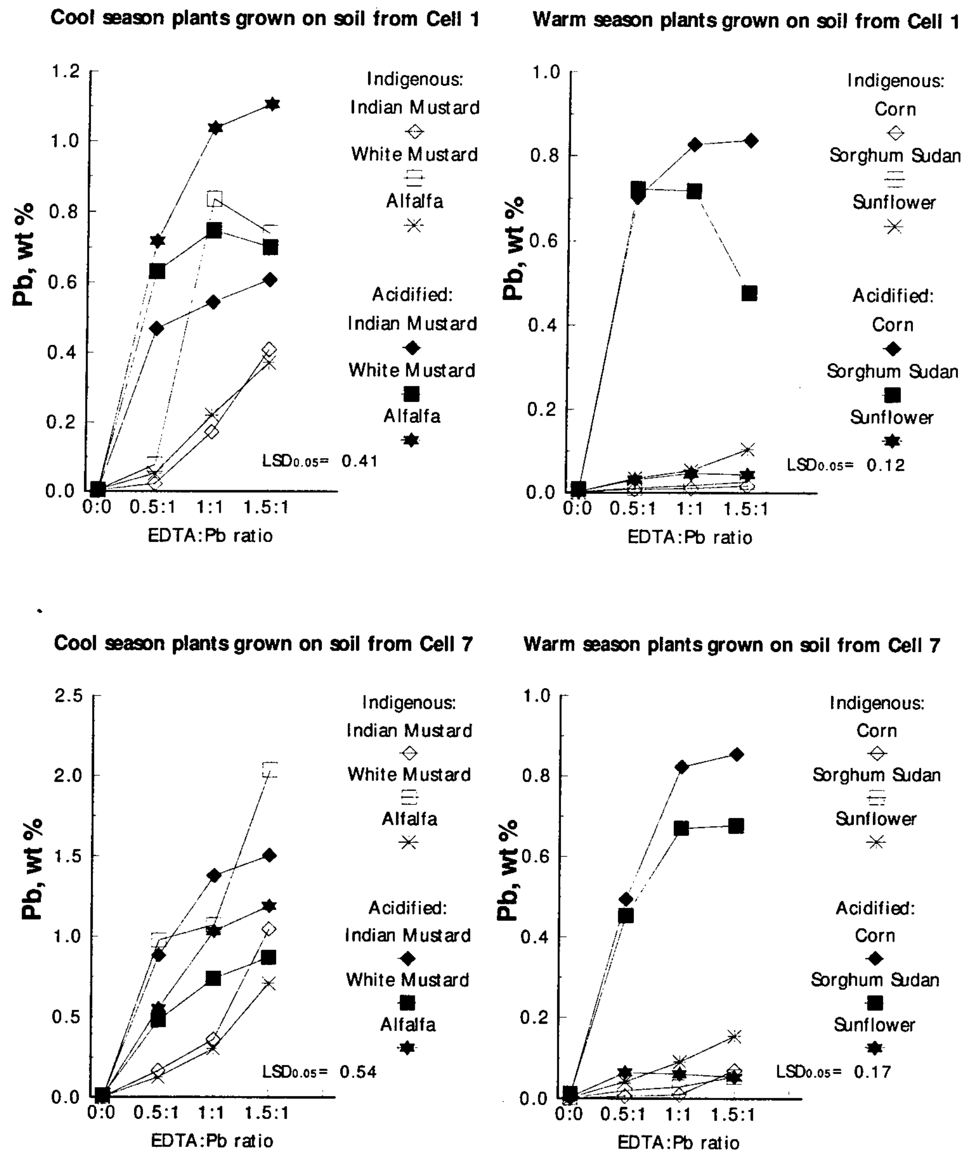


Figure 5-6

Plant Screening Study: Lead Concentrations in Plant Shoot Tissues

well to results produced when the plants are at a full vegetative biomass stage of growth, such as those reported in this study.

Of the cool season crops (Indian mustard [*Brassica juncea* L.], white mustard [*Brassica hirta* L.], and alfalfa [*Medicago sativa* L.]), alfalfa accumulated the highest concentration of lead in shoot tissue when grown in soil from Cell 1 at soil pH of 5.5. However, alfalfa did not perform as well when grown in soil from Cell 7. In addition, alfalfa was found to establish slowly and did not produce a large volume of biomass, so alfalfa was not studied further.

After alfalfa, white mustard (*Brassica hirta* L.) showed the greatest capacity for lead uptake when grown in soil from Cell 1 (without soil acidification). White mustard also accumulated more lead in its tissues than the other plant species planted in Cell 7 soil under optimum treatment conditions, which were for white mustard an EDTA-to-lead ratio of 1.5 without soil pH adjustment. Under other treatment configurations, white mustard performed as well as the other cool season species. Although lead uptake increased in white mustard at the 1.5 chelate ratio in Cell 7 soil, this same increase was not observed in Cell 1 soil. The recommended treatment configuration for Cell 1 soil is an EDTA-to-lead ratio of 1.0 without soil pH adjustment.

During the Plant Screening Study, the average lead concentration in white mustard was 1.5% by weight, with lead concentrations as high as 2.4% in individual replicates. This level was generally higher than that found by other investigators. Blaylock et al. [ref. 18] reported lead concentrations of 1.6% with Indian mustard while using EDTA. However, this result was obtained in soil recently amended with lead carbonate, which may not be a good simulation of lead-contaminated soil under field conditions. In soil taken from an actual lead-contaminated site (1,200 mg lead/kg), Indian mustard only accumulated lead up to 0.15% after soil amendment addition.[ref. 18] In contrast, we obtained lead concentrations in Indian mustard ten times (1.5%) the concentration achieved by Blaylock et al.[ref. 18] despite the fact that the lead in the SFAAP soil was deposited some 50 years ago.

The plant-available lead content in soil samples taken from the cool season crop treatments showed an increase in plant-available lead with increasing EDTA concentrations for alfalfa

(Table 5-4), white mustard (Table 5-5), and Indian mustard (Table 5-6). The concentrations of plant-available lead in acidified soil were slightly lower than in non-acidified soil. Although higher amounts of applied EDTA increased the plant-available lead concentrations, this provided little advantage for plant uptake at the highest EDTA concentrations (Figure 5-6). Therefore, EDTA should not be applied in EDTA/lead ratios higher than 1.0 since this would only add to project cost and would likely result in carry-over EDTA which might damage crops or promote metal leaching. Consequently, recommended treatment for white mustard is an EDTA-to-lead molar ratio of 1.0 without soil pH adjustment.

The best warm and cool season species (corn and white mustard) in the control groups were analyzed post-harvest for phosphorus (P) to determine whether the existing soils were providing sufficient P for good plant growth (Table 5-7). The control groups were not treated with chelates. Although the phosphorus levels in the corn were marginally adequate, neither plant species showed visible signs of phosphorus deficiency. Phosphorus application rates for the Foliar Application Study (discussed below) were based on these analyses.

5.3.2 Foliar Application Study

The purpose of the Foliar Application Study was to determine the phosphate fertilizer application level which would:

- Enhance biomass growth
- Maximize lead uptake
- Ameliorate lead toxicity to plants

Although phosphorus concentrations in the corn increased slightly with application of foliar P, the application did not enhance biomass production in Cell 1 or Cell 7 soil (Table 5-8). A slight increase in lead, nickel, and zinc uptake was observed for corn grown in Cell 1 soil (Table 5-8). However, the opposite was observed for corn grown in Cell 7 soil, with a slight decrease in lead uptake occurring when phosphorus was foliarly applied. Phosphorus application to white mustard resulted in considerable foliar injury, to the point of almost complete kill, so it was not possible to determine any benefit. Since there was little or no

Table 5-4

Plant Screening Study: Plant-Available Lead in Soil After EDTA Application and Harvest of Alfalfa Crop

Molar Ratio of Chelate to Lead	Plant-Available Lead, mg/kg[1]			
	Cell 1 Soil		Cell 7 Soil	
	At Natural pH	Acidified to pH 5.5	At Natural pH	Acidified to pH 5.5
0.0	74	50	77	68
0.5	906	711	951	914
1.0	1,350	1,360	1,490	1,370
1.5	1,720	1,550	2,000	1,730
$LSD_{0.05}$[2]	193	101	124	155

1) The results are the mean of each treatment replicated in triplicate.
2) LSD $_{0.05}$ – Least significant difference at the 5% probability level.

Table 5-5

Plant Screening Study: Plant-Available Lead in Soil from Cells 1 and 7 After EDTA Application and Harvest of White Mustard Crop

Molar Ratio of Chelate to Lead	Plant-Available Lead, mg/kg[1]			
	Cell 1 Soil		Cell 7 Soil	
	At Natural pH	Acidified to pH 5.5	At Natural pH	Acidified to pH 5.5
0.0	60	52	67	58
0.5	1,080	973	1,340	1,190
1.0	1,300	1,220	1,710	1,560
1.5	1,800	1,500	2,040	1,870
$LSD_{0.05}$[2]	176	189	162	257

1) The results are the mean of each treatment replicated in triplicate.
2) LSD $_{0.05}$ – Least significant difference at the 5% probability level.

Table 5-6

Plant Screening Study: Plant-Available Lead in Soils from Cells 1 and 7 After EDTA Application and Harvest of Indian Mustard Crop

	Plant-Available Lead, mg/kg[1]			
Molar Ratio of Chelate to Lead	**Cell 1 Soil**		**Cell 7 Soil**	
	At Natural pH	**Acidified to pH 5.5**	**At Natural pH**	**Acidified to pH 5.5**
0.0	61	57	57	61
0.5	1,010	969	1,120	870
1.0	1,430	1,320	1,640	1,580
1.5	1,850	1,800	2,000	1,850
$LSD_{0.05}$[2]	52	194	78	91

1) The results are the mean of each treatment replicated in triplicate.
2) $LSD_{0.05}$ – Least significant difference at the 5% probability level.

Table 5-7

Plant Screening Study: Phosphorus (P) Concentrations in Soils After White Mustard and Corn Harvest, Without EDTA Application (Control)

Crop	**Soil From**	**Soil pH[1]**	**P Concentration[1] (mg P/kg soil)**
White Mustard	Cell 1	Natural pH	2,390
		Adjusted to pH 5.5	2,980
	Cell 7	Natural pH	2,280
		Adjusted to pH 5.5	2,000
	Mean		2,410
	$LSD_{0.05}$[2]		161
Corn	Cell 1	Natural pH	1,070
		Adjusted to pH 5.5	1,140
	Cell 7	Natural pH	823
		Adjusted to pH 5.5	1,100
	Mean		1,030
	$LSD_{0.05}$[2]		96

1) The results are the mean of each treatment replicated in triplicate.
2) $LSD_{0.05}$ – Least significant difference at the 5% probability level.

Table 5-8

Foliar Application Study: Effect of Foliar Phosphate Applications on Phosphorus and Metal Concentrations in Corn Grown in Soil Acidified to pH 5.5

	Concentration in Plant, (mg/kg plant tissue) [1,2]									
% P Applied	**From Cell 1**					**From Cell 7**				
	Biomass Yield (g)	**P**	**Pb**	**Ni**	**Zn**	**Biomass Yield (g)**	**P**	**Pb**	**Ni**	**Zn**
0.0	65	1,000	5,680	23	108	70	988	8,390	24	275
0.5	62	1,170	6,420	24	129	71	1,110	7,420	22	271
1.0	66	1,250	7,060	26	135	68	1,180	7,020	22	269
$LSD_{0.05}$[3]	NS[4]	52	101	NS	NS	NS	NS	124	NS	NS

1) All plants were harvested 3-4 days after amendment addition.
2) The results are the mean of each treatment replicated in triplicate.
3) $LSD_{0.05}$ – Least significant difference at the 5% probability level.
4) NS - Not significant. Analysis of variance showed that differences between means of treatments were not significant at the 5% probability level.

biomass enhancement with corn and since the only effect on lead uptake was in soil from Cell 1, foliarly applied P was not used in any of the subsequent studies. The foliar application did not appear to affect the concentrations of plant-available lead in the soil (Table 5-9).

5.3.3 Soil Leaching Study

During the Soil Leaching Study, the recommended treatment regimes (i.e., best plants, chelate levels, and pH levels) from the Plant Screening Study were used to examine:

- Movement of lead and EDTA through the soil column.
- Whether chelate application would induce leaching of solubilized lead.
- The effect of lead and residual EDTA on subsequent plant germination and growth.

To conduct the study, corn and white mustard crops were grown from seed in 6-inch-diameter by 30-inch-long PVC columns containing 16 to 17 kg of soil. After the plants had attained full vegetative biomass, but prior to the addition of soil amendments, the soil was sampled at depths of 0"-6", 6"-12", 12"-18", and 18"-30" and analyzed for lead, zinc, and nickel content (Table 5-10). Comparing the original bulk soil lead, zinc, and nickel concentrations (Table 5-1) with those found in the soil prior to adding the soil amendments (Table 5-10) suggests that the metals did not move down the soil columns as a consequence of natural leaching processes. Soil pH also did not appear to change, suggesting that plant growth did not influence soil pH (Tables 5-1 and 5-11). However, the considerable buffering capacity of these soils may have been sufficient to negate any acidifying effect of plant root exudates. Analyses of the plant roots collected prior to soil amendment addition suggest the plants did take up small quantities of lead during the growing period (Table 5-12).

After the soil amendments were added and the crops harvested (three days later), the soil in each column was sampled again. The post-harvest soil analyses indicated that the total lead and zinc concentrations in the top 12 inches of both soils was somewhat lower than that found prior to soil amendment addition (Table 5-10). Most of these differences were statically significant. These results indicate that the plants were removing lead from the soil. Slight decreases in the nickel and zinc concentrations were also observed.

Table 5-9

Foliar P Application Study: Plant-Available Lead in Soils After Corn Harvest

	Soil from Cell 1[1]		Soil from Cell 7[1]	
% P Applied	**Plant-Available Lead (mg/kg)**	**Soil pH After Harvest**	**Plant-Available Lead (mg/kg)**	**Soil pH After Harvest**
0.0	1,310	6.3	1,780	6.9
0.5	1,260	6.2	1,490	6.7
1.0	1,370	6.5	1,500	7.0
$LSD_{0.05}$[2]	NS[3]	NS	59	NS

1) The results are the mean of each treatment replicated in triplicate.
2) $LSD_{0.05}$ – Least significant difference at the 5% probability level.
3) NS - Not significant. Analysis of variance showed that differences between means of treatments were not significant at the 5% probability level.

Table 5-10

Soil Leaching Study: Average Metal Concentrations in the Soil Columns After Growing the 1st Crop Both Before and After Soil Amendment Addition

Metal Concentrations in Soil Containing Corn[1]						
Soil Depth	Soil from Cell 1			Soil from Cell 7		
	Prior to Adding Soil Amendments	After Adding Soil Amendments	$LSD_{0.05}$[2]	Prior to Adding Soil Amendments	After Adding Soil Amendments	$LSD_{0.05}$[2]
Lead, mg/kg						
0"-6"	2,510	2,400	NS[3]	3,490	3,300	77
6"-12"	2,430	2,330	NS	3,500	3,380	56
12"-18"	2,610	2,420	92	3,420	3,410	NS
18"-30"	2,580	2,580	NS	3,480	3,430	NS
$LSD_{0.05}$[2]	NS	111		NS	31	
Nickel, mg/kg						
0"-6"	24	19	NS	33	23	NS
6"-12"	22	17	NS	30	20	NS
12"-18"	20	20	NS	30	21	NS
18"-30"	19	18	NS	27	22	NS
$LSD_{0.05}$[2]	NS	NS		NS	NS	
Zinc, mg/kg						
0"-6"	104	114	NS	270	223	22
6"-12"	118	98	7	279	210	16
12"-18"	112	102	NS	260	241	NS
18"-30"	115	100	8	259	226	21
$LSD_{0.05}$[2]	NS	9		NS	NS	
Metal Concentrations in Soil Containing White Mustard[1]						
Soil Depth	Soil from Cell 1			Soil from Cell 7		
	Prior to Adding Soil Amendments	After Adding Soil Amendments	$LSD_{0.05}$[2]	Prior to Adding Soil Amendments	After Adding Soil Amendments	$LSD_{0.05}$[2]
Lead, mg/kg						
0"-6"	2,603	2,380	56	3,500	3,230	101
6"-12"	2,550	2,210	68	3,460	3,320	56
12"-18"	2,600	2,500	NS	3,450	3,450	NS
18"-30"	2,530	2,470	NS	3,510	3,600	NS
$LSD_{0.05}$[2]	NS	52		NS	94	
Nickel, mg/kg						
0"-6"	23	23	NS	22	20	NS
6"-12"	21	10	6	25	15	NS
12"-18"	21	18	NS	37	17	9
18"-30"	24	23	NS	26	25	NS
$LSD_{0.05}$[2]	NS	2		4	6	
Zinc, mg/kg						
0"-6"	114	92	8	263	234	13
6"-12"	121	103	8	271	239	22
12"-18"	124	94	11	244	242	NS
18"-30"	110	91	NS	260	211	17
$LSD_{0.05}$[2]	NS	NS		9	NS	

1) The results are the mean of samples taken from duplicate columns.
2) $LSD_{0.05}$ – Least significant difference at the 5% probability level.
3) NS - Not significant. Analysis of variance showed that differences between means of treatment were not significant at the 5% probability level.

Table 5-11

Soil Leaching Study: Soil pH in the Soil Columns After Growing the 1st Crop, but Prior to Soil Amendment Addition

Soil Depth	Soil from Cell 1[1]		Soil from Cell 7[1]	
	Corn	White Mustard	Corn	White Mustard
	pH			
0"-6"	7.1	7.0	7.4	7.2
6"-12"	6.9	7.1	7.3	7.4
12"-18"	7.0	7.0	7.5	7.3
18"-30"	7.5	7.1	7.2	7.1
$LSD_{0.05}$[2]	NS[3]	NS	NS	NS

1) The results are the mean of samples taken from duplicate columns.
2) $LSD_{0.05}$ – Least significant difference at the 5% probability level.
3) NS - Not significant. Analysis of variance showed that differences between means of treatments were not significant at the 5% probability level.

Table 5-12

Soil Leaching Study: Metal Concentrations in Corn and White Mustard Roots After Growing the 1st Crop, but Prior to Soil Amendment Addition

Metal	Soil from Cell 1[1]		Soil from Cell 7[1]	
	Corn	White Mustard	Corn	White Mustard
Lead, mg/kg	809	901	1,487	2,170
Nickel, mg/kg	12	8	19	26
Zinc, mg/kg	71	53	190	273

1) The results are the mean of samples taken from duplicate columns.

The post-harvest soil samples were also analyzed for plant-available lead. The overall data for water-soluble lead at each depth (Table 5-13) indicates solubilization of lead down to 18 inches in the column, but little below the 18-inch level, depending on which crop was grown. For columns containing corn in Cell 1 soil, lead concentrations increased down to 18 inches, apparently due either to movement of EDTA with subsequent solubilization of lead at the wetting front, or movement of solubilized lead from the upper soil layers. There was an incremental increase in EDTA concentrations down to 18 inches which did not completely correspond to the amount of lead present. This EDTA may have been complexed with elements other than lead (e.g., calcium, iron, or aluminum), which would form a neutral, water-soluble complex subject to downward movement. However, this would have no effect on lead movement once the EDTA was so complexed. This may have significance for subsequent crops since EDTA may be phytotoxic. EDTA may slowly dissociate from the aforementioned aluminum, calcium, or iron complexes and damage the emerging seedling directly, or it may re-form a plant-available complex with lead which would eventually be phytotoxic to the growing plant.

It should be noted that the procedure used to analyze the EDTA in soil only indicates the amount of water-soluble EDTA present. Additional EDTA may be present in water-insoluble forms. Very little leachate was collected from the soil column and only a small percentage of the EDTA was found in the plants; therefore, it is likely that insoluble EDTA is bound in the soil matrix.

In contrast to the results with corn, for white mustard most of the plant-available lead remained in the top 12 inches of the soil column. Based on to soil samples taken 3 to 4 days after EDTA application, water-soluble EDTA also remained in the top 12 inches and tended to concentrate in the top 6 inches. Water-soluble EDTA concentrations were higher than those found with corn in the top 12 inches. A material balance suggests that substantially more water-soluble EDTA remained in the soil at the end of the harvest period (Table 5-14). However, the molar ratio of plant-available lead to water-soluble EDTA remaining in the soil was in the range of 0.5 to 0.6 at the end of the first harvest period. This is the same range found in the Chelate Screening Study.

Table 5-13

Soil Leaching Study: Water-Soluble EDTA and Lead in Soil Columns at Field Capacity After Soil Amendment Addition and Harvesting of the 1st Crop[1]

Soil Depth (inches)	Soil from Cell 1[2]				Soil from Cell 7[2]			
	Corn		White Mustard		Corn		White Mustard	
	Water-Soluble EDTA (mg/kg soil)	Plant-Available Lead (mg/kg soil)	Water-Soluble EDTA (mg/kg soil)	Plant-Available Lead (mg/kg soil)	Water-Soluble EDTA (mg/kg soil)	Plant-Available Lead (mg/kg soil)	Water-Soluble EDTA (mg/kg soil)	Plant-Available Lead (mg/kg soil)
0"-6"	1,740	806	12,000	1,220	4,460	2,050	14,900	1,450
6"-12"	1,990	1,080	4,490	2,100	1,280	863	11,100	2,210
12"-18"	2,640	1,020	340	212	1,410	910	285	155
18"-30"	334	99	226	140	136	86	62	41
$LSD_{0.05}$[3]	180	44	177	78	152	53	24	93

1) The soil samples were taken three days after EDTA addition.
2) The results are the mean of samples taken from duplicate columns.
3) $LSD_{0.05}$ – Least significant difference at the 5% probability level.

Table 5-14

Soil Leaching Study: Percent of Water-Soluble EDTA Remaining in the Soil Columns After Treatment and Harvesting the 1st Crop

	Percent of Total EDTA Added Remaining in a Water-Soluble Form[1] (Weight % of Total EDTA Added to Each Soil Column During Treatment)[2]			
Soil Depth (inches)	**Soil from Cell 1**		**Soil from Cell 7**	
	Corn	**White Mustard**	**Corn**	**White Mustard**
0"-6"	2.4%	16.3%	4.4%	14.8%
6"-12"	2.7%	6.1%	1.3%	11.0%
12"-18"	3.6%	0.5%	1.4%	0.3%
18"-30"	0.2%	0.1%	0.1%	0.1%
$LSD_{0.05}$[3]	0.4%	0.2%	1.0%	2.1%

1.) Water-insoluble forms of EDTA may be present in the soil; therefore, these figures may not reflect the total amount of EDTA present in the soil.
2.) Total amount of EDTA added to soil in columns: Cell 1 soil - 74,000 mg; Cell 7 soil - 100,600 mg.
3.) $LSD_{0.05}$ – Least significant difference at the 5% probability level.

In addition to the soil analysis above, TVA conducted a limited number of analyses of the plant tissues. These analyses suggest that plants were taking up EDTA, and that the corn was taking up more EDTA than the white mustard (EDTA concentration in corn was 11%; EDTA concentration in white mustard was 4%). These factors, combined with the soil analyses for lead and EDTA, support literature-based propositions which suggest that crops tend to take up EDTA and lead in one of two ways. The proposed mechanisms are:

1) The metal-chelate complex moves to the root by diffusion and is absorbed intact by the plant.

2) The metal-chelate complex moves to the root by diffusion whereupon the metal is released at the root surface and is then taken up by the plant. The chelate then complexes with another metal ion, and this process is then repeated.

Both pathways have been widely reported.[ref. 19] These pathways are thought to be crop dependent. If it is assumed that corn takes up both lead and EDTA via the first pathway, this may explain the lower concentrations of water-soluble EDTA in the soil surrounding the corn. Similarly, if it is assumed that white mustard follows the second pathway, this may explain the higher concentrations of water-soluble EDTA in the top 6 inches of the soil column and the reason it tends to remain within the plant root zone.

Three days (72 hours) after soil acidification, Cell 1 soil did not return to the original pH of 7.0, and at the lower depths very little recovery occurred (Table 5-15). This may have been due to the lower buffering capacity of Cell 1 soil compared to Cell 7 soil, which showed better recovery to the natural pH of 7.3, at least in the upper soil layers. Anaerobic conditions and compaction which can occur at the lower soil depths in this type of soil column study may have suppressed microbial degradation of the acetic acid. Microbial death due to the presence of acetic acid or solubilized lead would have resulted in reduced degradation of acetic acid. Since acetic acid was not used in conjunction with the chelate for white mustard, soil pH was not lowered. However, a slight increase in pH was seen in Cell 1 soil due to the addition of the chelate. This was not observed on Cell 7 soil due to the higher buffering capacity of this soil.

Table 5-15

Soil Leaching Study: Soil pH in the Soil Columns 72 Hours After Soil Amendment Addition and Harvesting of the 1st Crop

Soil Depth	Soil from Cell 1		Soil from Cell 7	
	Corn	White Mustard	Corn	White Mustard
	pH[1]			
0"-6"	6.6	7.6	7.0	7.2
6"-12"	6.2	7.4	6.9	7.4
12"-18"	5.9	7.6	5.9	7.3
18"-30"	5.5	7.5	5.8	7.1
$LSD_{0.05}$[2]	0.5	NS[3]	0.4	NS

1) The results are the mean of samples taken from duplicate columns.
2) $LSD_{0.05}$ – Least significant difference at the 5% probability level.
3) NS - Not significant. Analysis of variance showed that differences between means of treatments were not significant at the 5% probability level.

The lead concentrations in the shoots of both crops increased upon the addition of the soil amendments (Table 5-16). The metal concentrations found in the treated crops were similar to those observed in corn and white mustard in the Plant Screening Study (Section 5.3.1). This data, combined with the pre- and post-harvest soil analyses (Table 5-10), indicate the plants were removing lead from soil.

Analysis of the crop roots shows that the addition of soil amendments increased the metals concentrations in the roots (Table 5-17). However, lead concentrations in the roots were only about 10 to 20 percent of the concentration in the shoots. These results suggest that the EDTA induced xylem transport of lead from the root to the shoot with little storage in the root. The xylem is a vascular system that conducts water from the roots, through the plant stem, and up into the leaves. These results are consistent with those of Huang et al.[ref. 6], which also confirms that EDTA enhances xylem transport of lead to the shoots.

When a scanning electron microscope (SEM) was used to map the lead concentrations on corn shoots, the highest amount of lead was found in the leaves. Little or no lead was detected in the stems. A digital dot map was created to assess the relative abundance of lead throughout the leaf, (Figure 5-7). The lead was found to be evenly distributed throughout the leaf and not associated with any particular leaf structure. These results suggest that EDTA-solubilized lead is transported through the stem in the xylem with little or no movement into or accumulation in the surrounding stem cells. When the water carrying the lead in the xylem reaches the leaf, the lead is then distributed throughout the leaf and accumulates in the leaf cells.

A sequential extraction procedure was performed on bulk soil from both Cell 1 and Cell 7 to determine the forms of soil metals before and after amendment addition. This procedure showed that lead solubility in the Sunflower soil is controlled primarily by the carbonate and hydrous oxide mineral fraction of the soil (Table 5-18 and 5-19). The organic fraction was of lesser importance. These findings agreed with other published studies[refs. 20,21] which show that lead solubility in most mineral soils will be limited by the less soluble fractions of the soil, and in particular, the hydrous oxide fraction. A significant portion of lead also was associated with the carbonate fraction. This correlates with the slightly alkaline pH (7.0-7.3) of the soils. The significant organic content of the soil (Table 5-1) accounted for the amount of lead complexation observed with organics.

Table 5-16

Soil Leaching Study: Metal Concentrations in Corn and White Mustard Shoots After Soil Amendment Addition and Harvesting of the 1st Crop

Analysis	Soil from Cell 1[1]		Soil From Cell 7[1]	
	Corn	White Mustard	Corn	White Mustard
	Controls With No Soil Amendment Addition			
Crop Yield, g	65	21	71	26
Lead, mg/kg	31	32	34	49
Nickel, mg/kg	9	5	10	8
Zinc, mg/kg	95	103	102	117
	With Soil Amendments Added			
Crop Yield, g	64	20	69	24
Lead, mg/kg	8,510	12,580	8,380	16,330
Nickel, mg/kg	10	10	8	9
Zinc, mg/kg	127	114	159	132

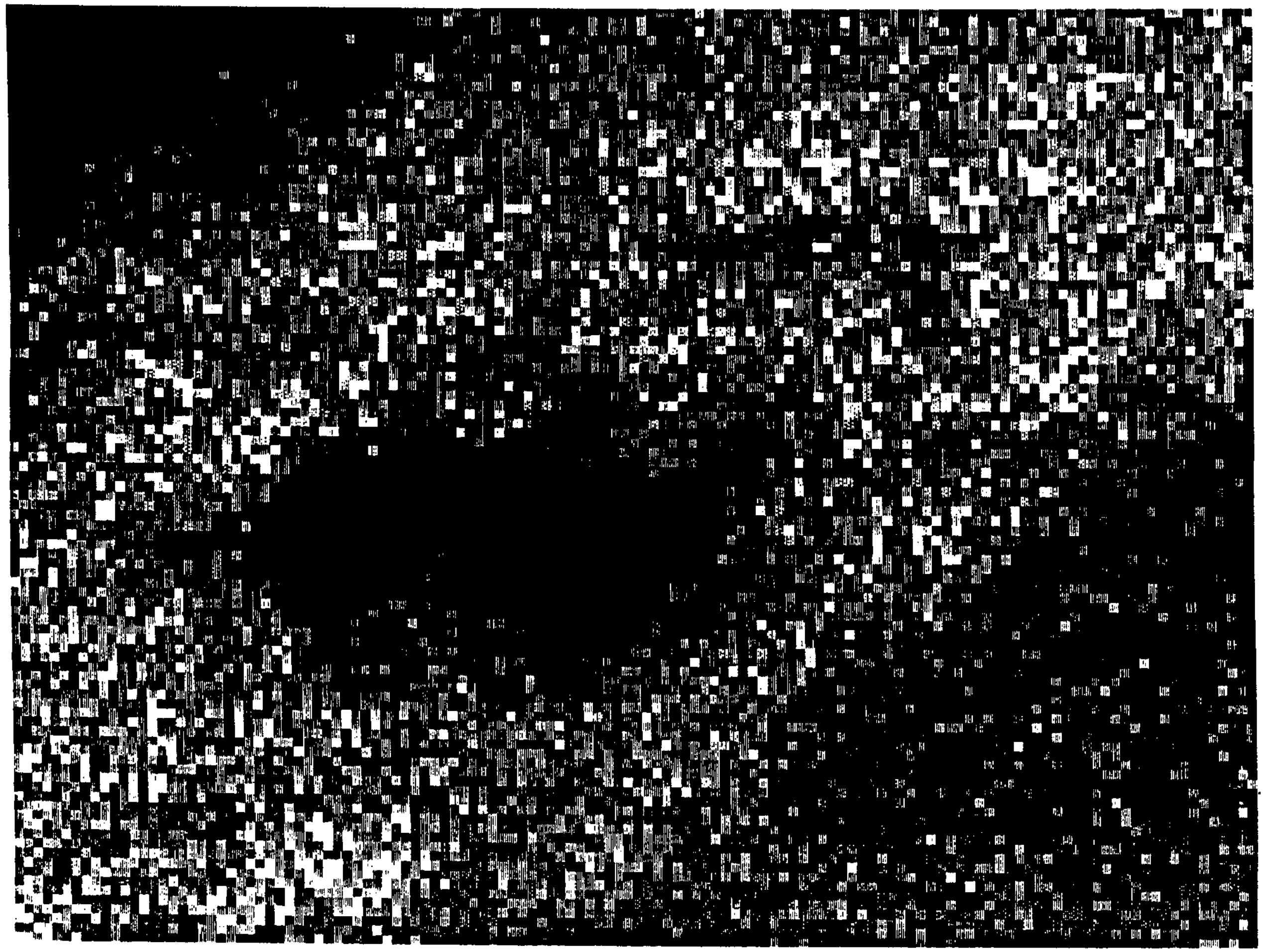
1) The results are the mean of samples taken from duplicate columns.

Table 5-17

Soil Leaching Study: Metal Concentrations in the Roots of the 1st Crops After Harvesting the Crops

Metal	Soil from Cell 1[1]		Soil From Cell 7[1]	
	Corn	White Mustard	Corn	White Mustard
	Controls With No Soil Amendment Addition			
Lead, mg/kg	779	987	1,450	2,100
Nickel, mg/kg	10	10	22	25
Zinc, mg/kg	82	54	223	280
	With Soil Amendments Added			
Lead, mg/kg	1,161	1,260	1,220	2,320
Nickel, mg/kg	29	21	46	37
Zinc, mg/kg	297	100	444	396

1) The results are the mean of samples taken from duplicate columns.



Note: Light portions of the figure represent lead concentrations within the leaf's surface and cross section. The dark circle in the center is a plant vein.

Figure 5-7

Scanning Election Microscope View of Leaf Surface and Cross Section

Table 5-18

Soil Leaching Study: Sequential Metal Analysis of Soil from Cell 1

Metal Analyses						
Type of Analyses	**Lead**		**Nickel**		**Zinc**	
	Concentration (mg/kg)	**Wt. % of Total Extracted**	**Concentration (mg/kg)**	**Wt. % of Total Extracted**	**Concentration (mg/kg)**	**Wt. % of Total Extracted**
Exchangeable	47	2%	1	3%	1	1%
Carbonate	769	30%	1	3%	11	10%
Fe & Mn oxide	1,210	47%	12	41%	43	38%
Organic	398	15%	4	14%	3	3%
Residual	147	6%	11	38%	57	50%
Total extracted by procedure	2,570	100%	29	99%	114	102%
Total soil analysis	2,530[1]		21		112	

1) Hydrogen peroxide--nitric acid digestion.

Table 5-19

Soil Leaching Study: Sequential Metal Analysis of Soil from Cell 7

Type of Analyses	Metal Analyses					
	Lead		Nickel		Zinc	
	Concentration (mg/kg)	Wt. % of Total Extracted	Concentration (mg/kg)	Wt. % of Total Extracted	Concentration (mg/kg)	Wt. % of Total Extracted
Exchangeable	99	2%	1	2%	3	1%
Carbonate	1,280	32%	2	2%	40	15%
Fe & Mn oxide	1,760	44%	17	40%	127	47%
Organic	593	15%	7	17%	16	6%
Residual	305	8%	15	35%	68	25%
Total extracted by procedure	4,040	101%	42	96%	269	94%
Total soil analysis	3,440[1]		28		202	

1) Hydrogen peroxide--nitric acid digestion.

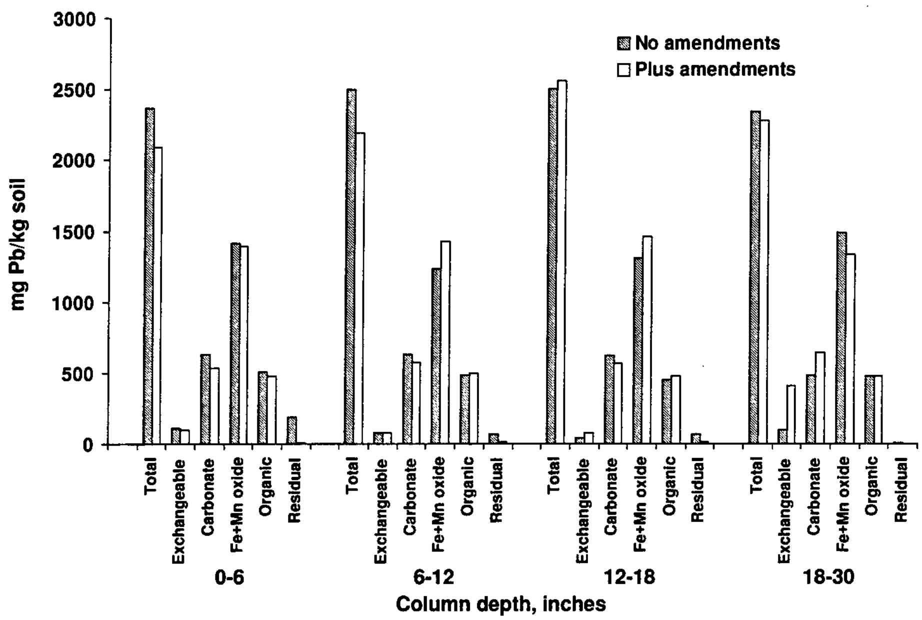
Similarly, the hydrous oxide fraction accounted for a significant portion of bound nickel and zinc. Very little of the nickel and zinc were complexed with the carbonate or the organic fractions, but the residual fraction accounted for about a third of the nickel and up to half of the zinc in the bound fractions of each soil. These findings are in agreement with Behel[ref. 22] who obtained similar results using geochemical modeling to predict metal equilibria in metal-contaminated soils.

Amendment additions had little effect on the degree of metal association with the various soil fractions (Appendix E and Figures 5-8 to 5-13). There was a quantitative reduction in the amount of lead associated with each fraction or "pool", at each depth of 0"-6', 6"-12", 12"-24", and 24"-36", which followed amounts removed through plant uptake. However, the overall equilibrium of metals among the various soil components remained relatively unchanged after soil amendment additions, with little conversion of metals from one fraction to another. This indicates that metals, and lead in particular, in these soils are normally highly unavailable to plants, and that little change in metal solubility would be likely to occur through natural processes. This indicates that this soil would contribute minimally to further contamination of the environment if left undisturbed. These findings further illustrate that phytoextraction may be a viable and effective means to remediate recalcitrant metals, such as lead, which otherwise would remain fixed in the soil.

A second crop was attempted during the Soil Leaching Study. However, other than the controls, crops planted during the second growing period either failed to germinate or died. The crops in the treated columns were replanted, but these plants also died. To determine why the crops were failing, TVA conducted germination tests.

The purpose of the germination test was to determine if the poor germination during the second growing period was the result of excess sodium (introduced as a tri-sodium salt of EDTA), residual chelate, solubilized lead, or a combination of these factors. Two soils were used during these tests. The first soil was from Cell 7. The second soil was an Epping silt loam soil from Nebraska. The Epping loam has been used in numerous TVA studies and has been well-characterized.. The Eppling loam was very similar chemically and physically to the soils from SFAAP, but contained no lead.

Extractable Lead in Soil from Cell 1 after Corn Grown



Extractable Lead in Soil from Cell 7 after Corn Grown

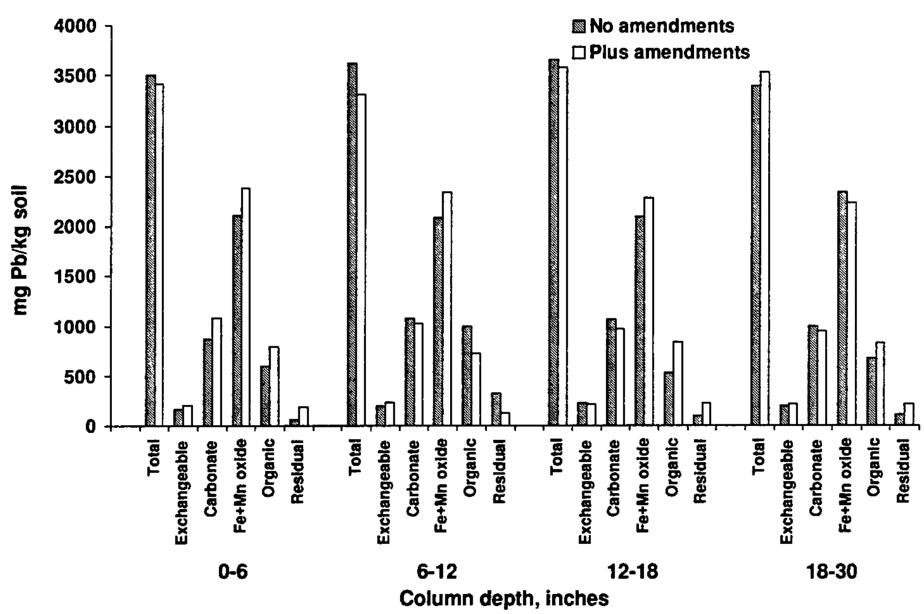
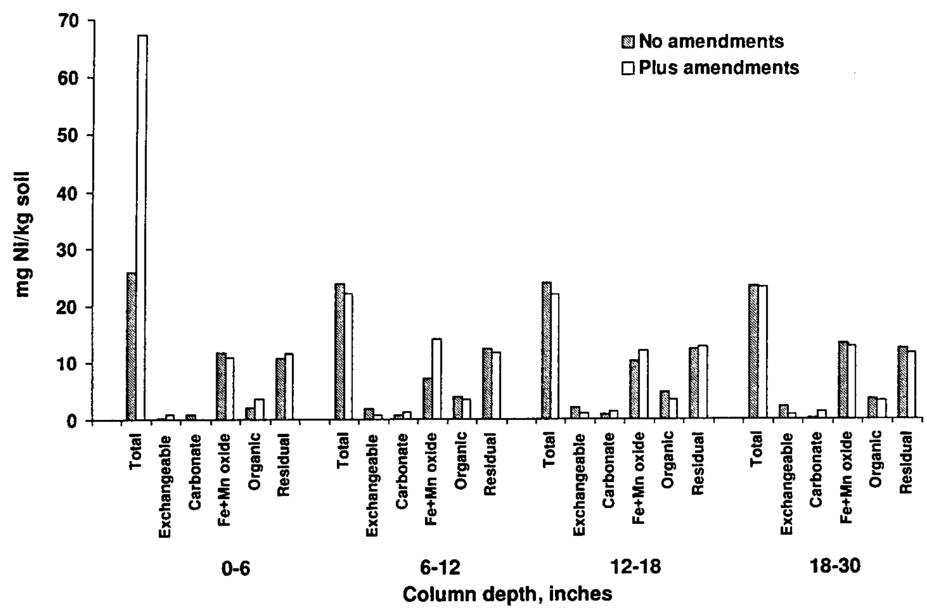


Figure 5-8

Soil Leaching Study: Sequentially Extractable Lead in Soils After Growing, Treating, and Harvesting Corn

Extractable Nickel in Soil from Cell 1 after Corn Grown



Extractable Nickel in Soil from Cell 7 after Corn Grown

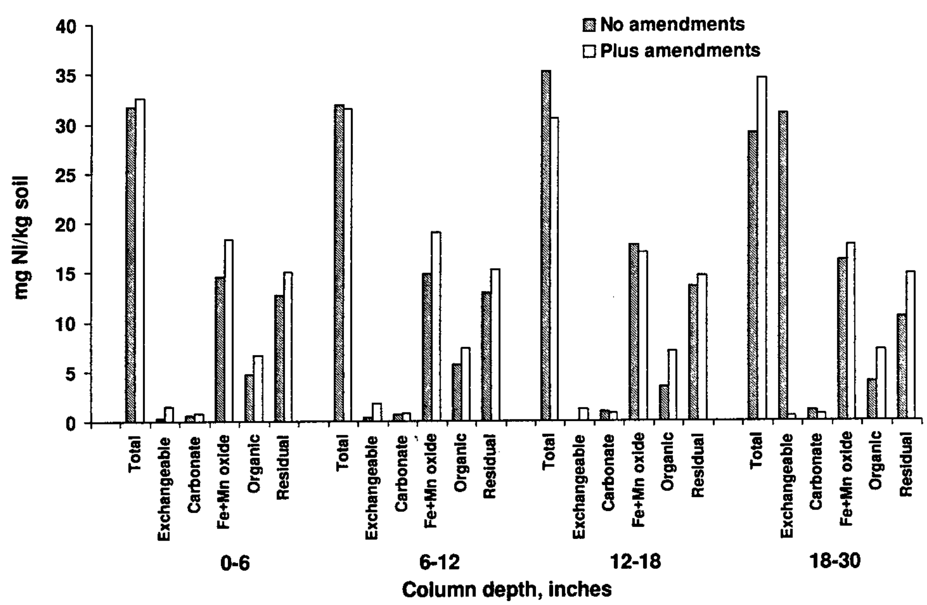
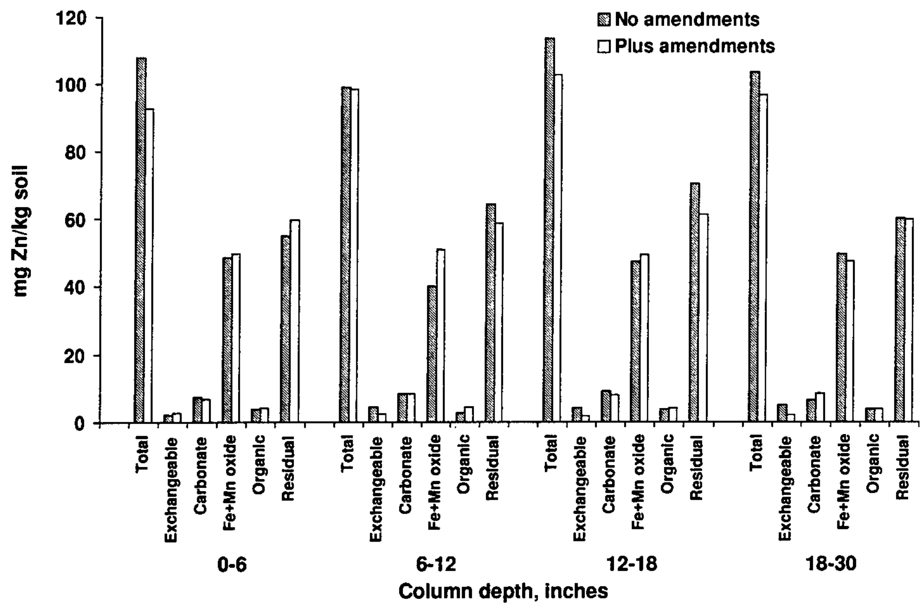


Figure 5-9

Soil Leaching Study: Sequentially Extractable Nickel in Soils After Growing, Treating, and Harvesting Corn

Extractable Zinc in Soil from Cell 1 after Corn Grown



Extractable Zinc in Soil from Cell 7 after Corn Grown

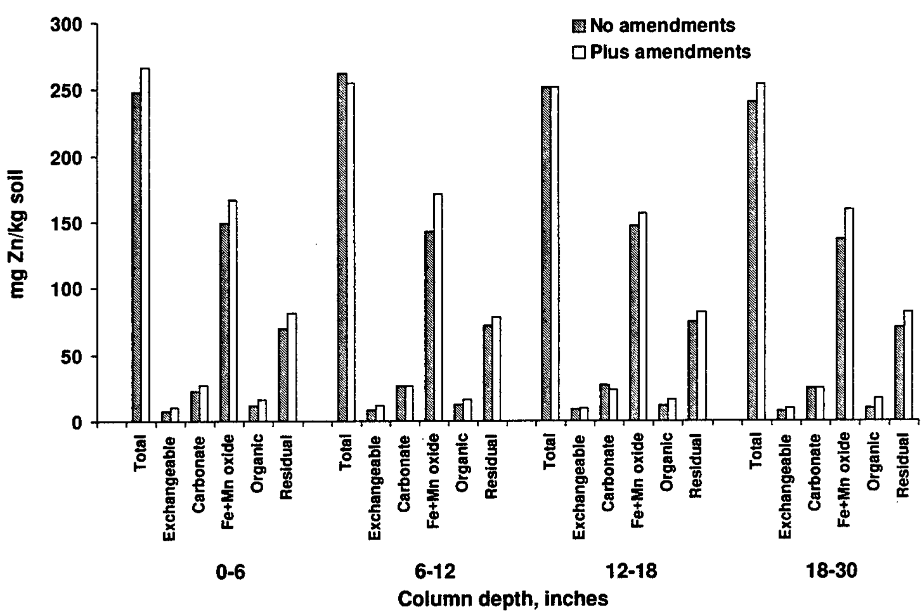
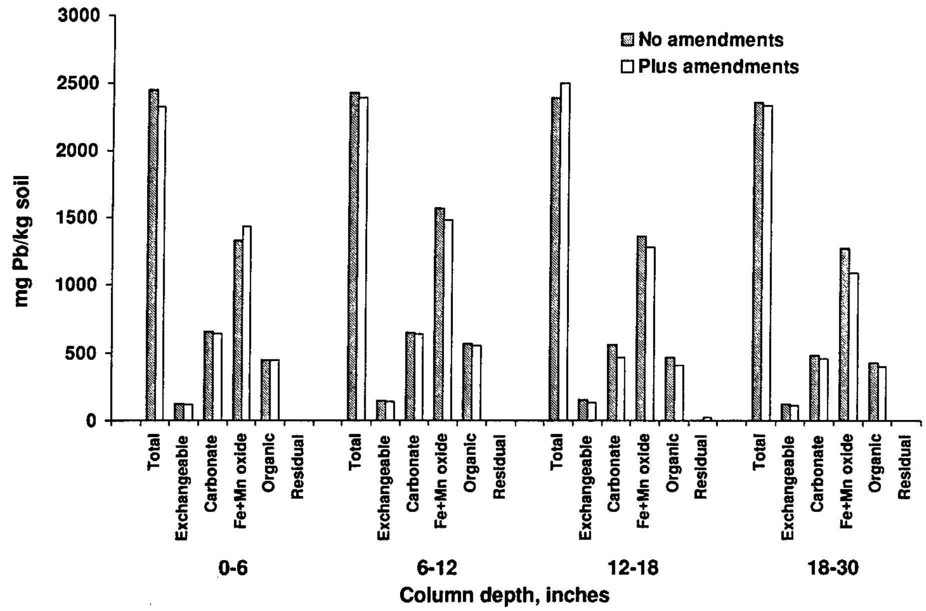


Figure 5-10

Soil Leaching Study: Sequentially Extractable Zinc in Soils

After Growing, Treating, and Harvesting Corn

Extractable Lead in Soil from Cell 1 after White Mustard Grown



Extractable Lead in Soil from Cell 7 after White Mustard Grown

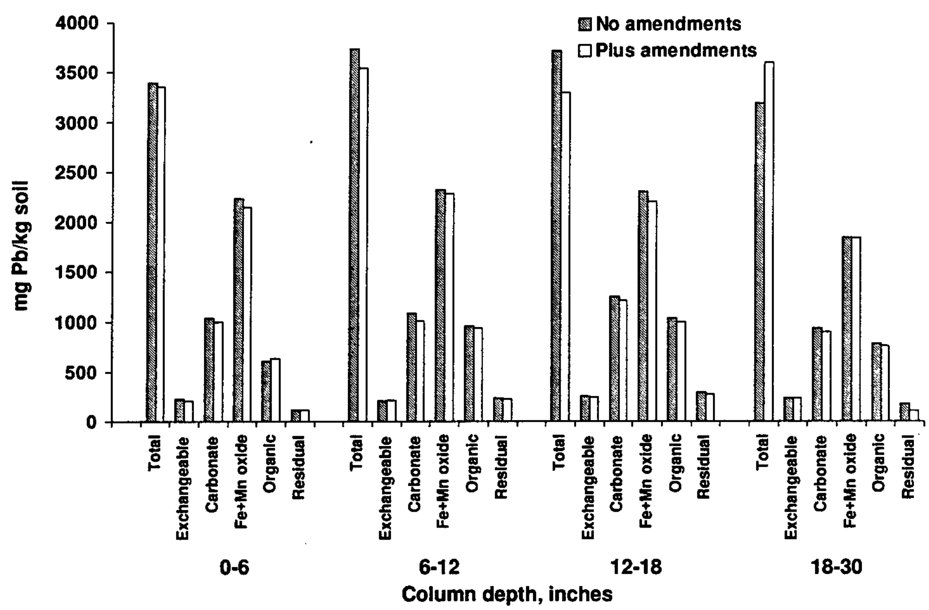
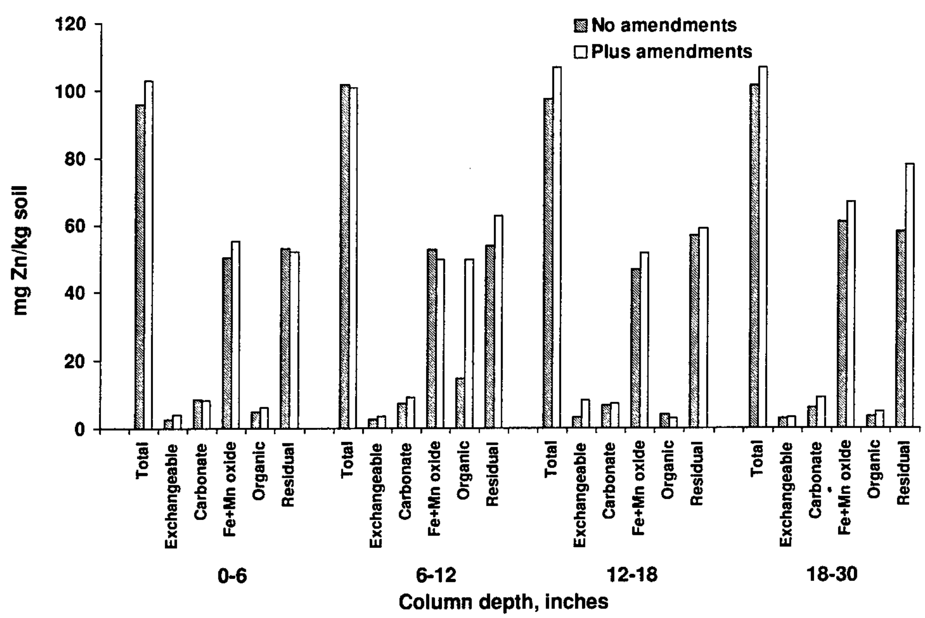


Figure 5-11

Soil Leaching Study: Sequentially Extractable Lead in Soils After Growing, Treating, and Harvesting White Mustard

Extractable Zn in Soil from Cell 1 after White Mustard Grown



Extractable Zn in Soil from Cell 7 after White Mustard Grown

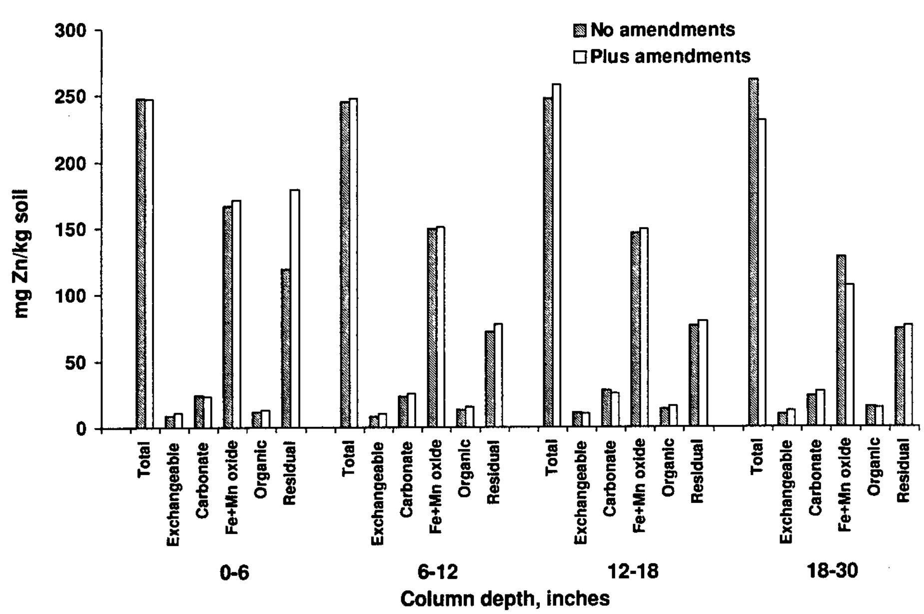
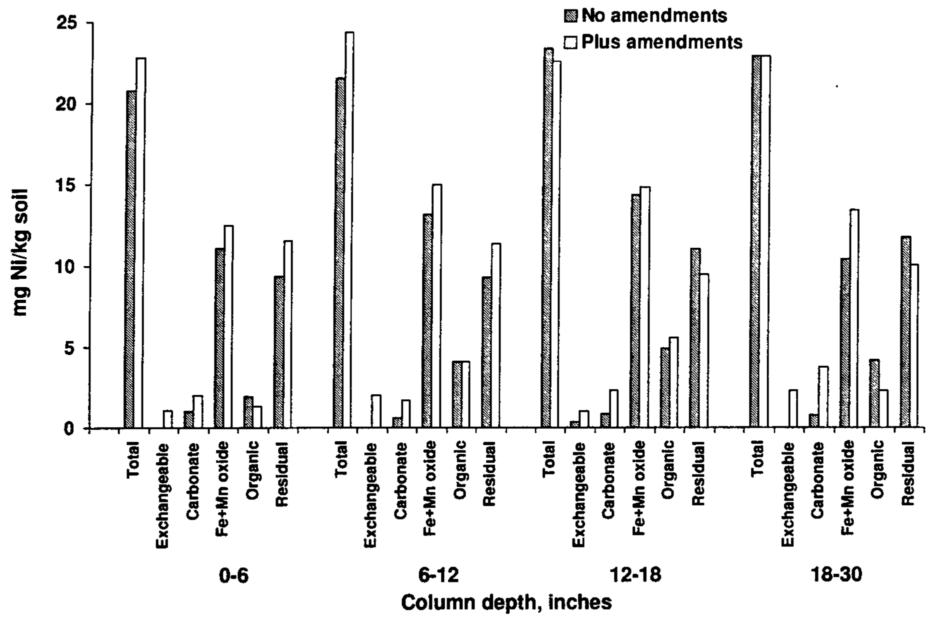


Figure 5-12

Soil Leaching Study: Sequentially Extractable Nickel in Soils After Growing, Treating, and Harvesting White Mustard

Extractable Nickel in Soil from Cell 1 after White Mustard Grown



Extractable Nickel in Soil from Cell 7 after White Mustard Grown

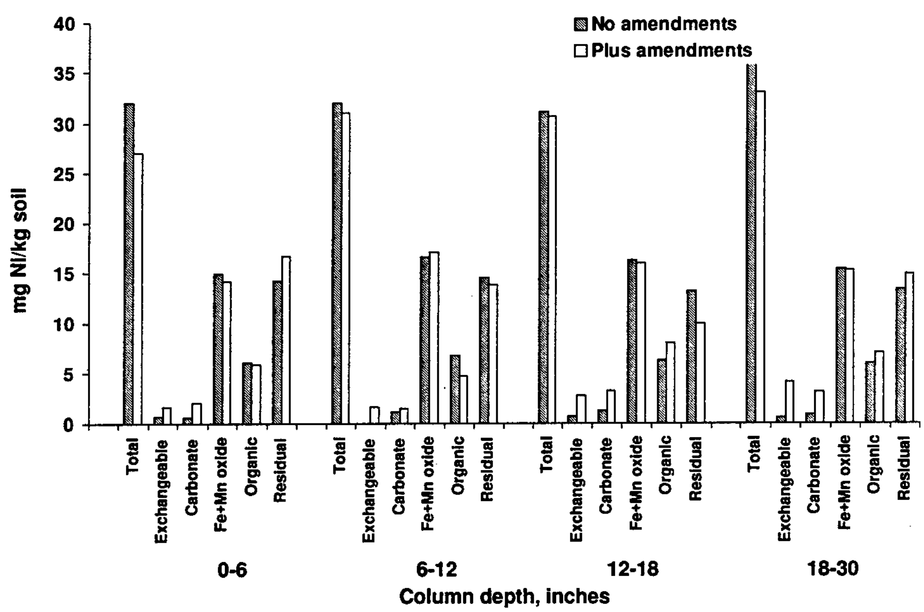


Figure 5-13

Soil Leaching Study: Sequentially Extractable Zinc in Soils After Growing, Treating, and Harvesting White Mustard

Test parameters were conducted with white mustard and consisted of:

- Sodium chloride and sodium nitrate applied to both soils at a sodium concentration which matched that of the EDTA originally used (to test for inhibitory effect of sodium.)
- Potassium chloride and potassium nitrate applied to both soils at a concentration to match the sodium concentration (to test for and eliminate chloride and nitrate as the inhibitory agents).
- Tri-sodium and tri-potassium EDTA applied to both soils at concentrations matching those originally used in the Soil Leaching Study (to determine the inhibitory effect of EDTA).

When using the lead-free soil, the germination test results showed:

- A strong inhibitory effect of sodium, but not potassium, on seed germination and seedling survival. Only 4% of seeds germinated in soil treated with the sodium solutions. The seedlings subsequently died.
- A slight inhibitory effect of the potassium salts due to the concentration of salt in contact with the seed. About 90% of the seeds germinated. About 7% died shortly after emergence, for a survival rate of 83%.
- An almost complete inhibition of germination when using sodium EDTA. Surviving seedlings died within one week.
- Germination rate with potassium EDTA was about 80%. Another 10% seedling loss after germination reduced the survival rate to 70%.

In the lead-contaminated soil, germination and seedling survival was reduced by another 10%-20%, most likely due to soluble lead.

These results showed that seed germination may be improved by use of the potassium salt of EDTA rather than the sodium salt. Both EDTA and soluble lead were implicated in reduced seed germination and seedling survival. Additional work is needed to allay these problems (see Recommendations for Future Work, Section 6.3)

The collection of leachate during both the first and second growing periods was inhibited by the effect of sodium on the soil structure. It was apparent that the sodium was causing flocculation near the top of the soil column. This restricted water flow so that very little leachate reached the bottom of the column. Consequently, representative leachate samples could not be collected during the Soil Leaching Study.

In an attempt to overcome this problem, a Lysimeter Study was added to the project. To remove the sodium source, the Lysimeter Study was conducted with tri-potassium EDTA.

5.3.4 Lysimeter Study

The Lysimeter Study was designed to more accurately monitor EDTA and lead movement through the soil column. The Lysimeter Study experimental design was very similar to the design created for the Soil Leaching Study. For this study:

- One soil was used (Cell 7 soil)
- The study was conducted over one growing period
- Columns were planted with white mustard (i.e., grow white mustard and treat with a 1.0 molar ratio of EDTA/soil-borne lead at the natural soil pH)
- No controls were used

Although leachate samples were to be collected during the Lysimeter Study (Table 4-17), the low hydraulic conductivity of the heavy textured soil so severely restricted water movement that leachate samples could not be obtained.

Analysis of soil samples collected prior to soil amendment addition indicated that normal watering and plant growth did not cause lead or nickel to move through the soil column (Table 5-20). However, a slight increase in zinc concentration was noted at the lower depths.

The EDTA application appeared to influence lead, nickel, and zinc migration down to a depth of 12 inches. This is indicated by a slight decrease in metal concentrations in the soil samples taken between 0"-6" and slight increase occurring in the samples taken between 6"-12"

Table 5-20

Lysimeter Study: pH and Total Metal Concentrations in Soil Taken from Lysimeter Columns Growing White Mustard in Soil from Cell 7

	Pre-Harvest[1]				Post-Harvest[1]			
Depth	**pH**	**Lead (mg/kg)**	**Nickel (mg/kg)**	**Zinc (mg/kg)**	**pH**	**Lead (mg/kg)**	**Nickel (mg/kg)**	**Zinc (mg/kg)**
0"-6"	7.4	3,500	22	257	7.7	3,340	17	223
6"-12"	7.0	3,510	25	266	7.5	3,720	23	267
12"-18"	7.3	3,420	22	272	7.5	3,350	19	244
18"-30"	7.5	3,590	27	280	7.2	3,520	15	250
$LSD_{0.05}$[2]	NS[3]	NS	NS	9	NS	72	NS	14

1) The results are the mean of samples taken from duplicate columns.
2) $LSD_{0.05}$ – Least significant difference at the 5% probability level.
3) NS - Not significant. Analysis of variance showed that differences between means of treatments were not significant at the 5% probability level.

(Table 5-20). The lead concentrations did not appear to change below the 18-inch depth. As in the Soil Leaching Study, Cell 7 soil pH slightly increased with chelate application, with the greatest change occurring in the top 6 inches of soil.

Analysis of white mustard shoots and roots showed essentially the same amount and pattern of lead uptake experienced during the previous studies (Table 5-21).

5.3.5 Chelate Application Timing Study

The Chelate Timing Study was designed to determine if lead uptake could be enhanced by adding EDTA when water use by white mustard was at a maximum (i.e. during bolting and flowering). The white mustard crop took up approximately the same amount of lead during bolting but prior to flowering as it did during actual flowering, indicating that lead uptake was not effected by timing of application (Table 5-22). Therefore, EDTA may be applied throughout the bolting and flowering period without affecting the lead uptake efficiency of white mustard.

5.3.6 Harvest Timing Study

The Harvest Timing Study was designed to determine the time required for maximum lead accumulation by white mustard after EDTA has been added to the soil. This length of time has a direct bearing on the harvesting efficiency of white mustard. The treated plants become brittle as they dry out. Consequently, their leaves are subject to wind dispersion and the stalks and leaves may shatter during harvesting. Therefore, it is desirable to harvest the white mustard crop prior to the point that it becomes completely dry. Lead uptake increased significantly up to 48 hours after EDTA application and increased very slowly thereafter (Table 5-23). Therefore, white mustard can be harvested as early as 48 hours after an EDTA application to minimize wind dispersion and shattering of plants.

Table 5-21

Lysimeter Study: Pre- and Post-harvest Concentrations of Metals in the Shoots and Roots of White Mustard Grown in Soil from Cell 7

	Pre-Harvest[1]	Post-Harvest[1]	
Metal	**Metals in Shoots**		**$LSD_{0.05}$[1]**
Lead, mg/kg	51	16,800	141
Nickel, mg/kg	6	11	4
Zinc, mg/kg"	91	127	20
	Metals in Roots		
Lead, mg/kg	670	1,770	276
Nickel, mg/kg	16	27	4
Zinc, mg/kg"	87	243	22

1) The results are the mean of samples taken from duplicate columns.
2) $LSD_{0.05}$ – Least significant difference at the 5% probability level.

Table 5-22

Timing of Chelate Application to Maximize Lead Uptake by White Mustard

Time of Application	Lead Concentration (Wt. %)
Before flowering	1.98
During flowering	2.03
$LSD_{0.05}$[1]	NS[2]

1) $LSD_{0.05}$ – Least significant difference at the 5% probability level.
2) NS - Not significant. Analysis of variance showed that differences between means of treatments were not significant at the 5% probability level.

Table 5-23

Time Required after Chelate Application for Maximum Lead Uptake by White Mustard

Harvest Time (hr)	Lead Conc. (Wt. %)[1]
24	1.63
48	1.89
72	1.94
96	1.90
108	2.01
$LSD_{0.05}$[1]	0.14

1) The results are the mean of samples taken from duplicate columns.
2) $LSD_{0.05}$ – Least significant difference at the 5% probability level.

5.4 Quality Assurance

The Quality Assurance Program used during this project is provided, in detail, in Appendix B. The reliability of the data was monitored through the use of quality control samples, as specified in this program and following EPA guidelines, wherever applicable. These quality control samples included analysis of method blanks, analysis of calibration standards, analysis of independently produced quality control samples, and analysis of matrix spikes. Method blanks were used to determine whether an analyte might be present in reagents or from laboratory equipment. Reanalysis of calibration standards throughout runs was used to monitor process stability. Analysis of independently prepared quality control samples was used to check for bias in calibration. Matrix spike samples were used to monitor matrix effects. Other measurements which are characterizations of physical or chemical properties, such as buffer curves and moisture release curves, are not amenable to quality control protocols. The data generated from the QC samples are retained with the records of analysis, as described in Appendix B, Section B.5.

During this project, there were no major problems detected in the QA system that negatively impacted the validity of the results.

SECTION 6.
CONCLUSIONS

6.1 Background

Phytoextraction appears promising as a cost-effective method for remediating soils contaminated with moderate levels of heavy metals (3,000-4,000 ppm lead). However, as an emerging technology, the methodology and process of applying phytoextraction are still being defined through demonstrations. Several issues remain to be addressed before phytoextraction is truly a viable process. Since lead tends to remain in the soil where it has been deposited, one challenge to lead remediation is the naturally low solubility of lead in soils, which prevents any significant uptake of lead by plants. A second limitation is the tendency of lead to accumulate within the root structures of most plants rather than moving to the shoots where it can be removed by harvesting.

These limitations are overcome if lead is solubilized during the remediation process. This is possible because soil acidifiers and chelates convert soil-borne lead into a water-soluble plant-available form which enhances its uptake and translocation to the shoots in large amounts.

The focus of this effort was to investigate the use of phytoextraction methods (soil application of acidifiers and chelates) to increase lead uptake and translocation from the soil to the aerial portions of plant species. The most important issues addressed in this document were improvements in chelate selection and use, the effect of soil pH adjustment, investigation of chelate persistence, selection of plant species, and investigating the potential for migration of chelates and solubilized lead beyond the root zone.

6.2 Study Results

6.2.1 Chelate Screening Study

The efficiency of three chelates (EDTA, CDTA, and EGTA) was evaluated during the Chelate Screening Study. To determine the amount of metal extracted by each chelate, two different

soils were treated with the chelates and then extracted with water. The soil treatments consisted of three chelate concentrations in soils either acidified to pH 5.5 or left at the natural pH. Water extracted from the soils was analyzed for lead, cadmium, chromium, copper, nickel, and zinc. Where applicable, acetic acid was used to decrease the soil pH. The soil pH was also monitored over a 72-hour period to determine the time required for the treated soils to return to the natural pH.

Of the chelates tested, EDTA was found to be the most effective at extracting lead from soil. The EDTA solubilized an average of 60 percent of the soil total lead when applied at a rate of 15 mmole/kg. Soil acidification did not appear to impact EDTA effectiveness in either soil. The addition of acetic acid to the soils did not permanently affect soil pH. Instead, the soils gradually returned to the natural pH within 72 hours. CDTA was almost as effective as EDTA, but is more expensive.[Ref. 23] Therefore, EDTA was chosen for further study.

6.2.2 Chelate Application Study

During the Chelate Application Study, EDTA was applied to 24-inch-long columns of both soils in volumes of water calculated to bring soil moisture to 1.0 or to 1.5 times field capacity. About 55% of the chelate was recovered in soil from Cell 1 after 2 weeks, with similar recovery in the soil from Cell 7 after 4 weeks. In the soil from Cell 1, EDTA was found to a depth of 18 inches. Generally, chelate concentration decreased with depth and little EDTA was found below a depth of 18 inches. Minimal downward movement of EDTA in Cell 7 soil was observed, although higher concentrations were seen below depths of 18 inches when excess water (1.5 times field capacity) was added to the soils. These results suggested that chelate movement in the root zone (top two feet) can be minimized if the volume of EDTA solution applied is only enough to bring the soil to field capacity. The results reinforce the premise that the volume of EDTA solution applied should not exceed the field capacity of the root zone.

In all of the cases examined, EDTA remained in the soils four weeks after application.

6.2.3 Plant Screening Study

The Plant Screening Study test results indicated that the best warm season treatment parameters were:

- Use of a corn crop
- Soil adjustment to a pH of 5.5 using acetic acid
- A chelate application of 1.0 mole EDTA/mole soil lead

The best cool season treatment was:

- Use of a white mustard crop
- No adjustment of soil pH
- A chelate application of 1.0 mole EDTA/ mole soil lead

6.2.4 Foliar Application Study

The purpose of the Foliar Application Study was to determine if foliar phosphate fertilizer applications would enhance biomass growth, maximize lead uptake, or ameliorate lead toxicity to plants.

The corn crops did not receive a significant benefit from the foliar applications. Although lead, nickel, and zinc uptake increased slightly when growing corn in Cell 1 soil, lead uptake decreased in corn grown in Cell 7 soil. Although the applications slightly increased the phosphorus concentrations in the corn, the applications did not enhance corn biomass production in either Cell 1 or Cell 7 soil.

A foliar application was detrimental to white mustard. Application to white mustard resulted in considerable foliar injury to the point of almost complete kill.

Given that the benefits of foliar application to corn were minimal and that an application to white mustard would be counterproductive, foliarly applied phosphate was not used in any of the subsequent studies.

6.2.5 Soil Leaching Study

The results of the Soil Leaching Study indicated that lead solubilization was generally limited to the plant root zone (i.e., top two feet of soil). A small amount of EDTA moved to lower soil depths, and this was accompanied by a small increase in the soil plant-available (water-soluble) lead content. However, this EDTA may have complexed with other cations (e.g., calcium, iron, or aluminum) forming a neutral, water-soluble complex which could not solubilize additional lead. Therefore, the risk of leaching lead out of the root zone appears to be small as long as the bulk of the EDTA is retained within the root zone.

One way of limiting EDTA migration out of the root zone is to minimize the volume of EDTA solution added to soil. For this reason, it is recommended that the volume of solution used be limited to the amount required to bring the soil in the root zone to field capacity.

Attempts to grow a second crop of white mustard failed when the seeds did not germinate or the seedlings died shortly after germination. The addition of fresh soil to the columns (i.e., one-quarter inch soil added to the soil surface) improved germination, but subsequent seedling survival was poor. Tests were conducted to determine why the white mustard crops failed. These tests indicated the primary problems were the presence of excess EDTA and sodium in the soil. The excess sodium was introduced with a tri-sodium salt of EDTA. All subsequent tests were conducted with tri-potassium EDTA.

The excess sodium also caused flocculation near the top of the soil column which restricted water flow through the soil column. The low hydraulic conductivity of the soil also restricted water movement. Consequently, representative leachate samples could not be collected during the Soil Leaching Study. In an attempt to overcome this problem, a Lysimeter Study was added to the project.

6.2.6 Lysimeter Study

Although the Lysimeter Study was designed to monitor EDTA and lead movement through the soil columns, the low hydraulic conductivity of the soil so severely restricted water movement that leachate samples could not be collected. However, as in the Soil Leaching Study, soil analysis showed that EDTA did not appear to migrate below the root zone, and lead concentrations below the root zone did not appear to change.

6.2.7 Chelate Application and Harvest Timing Studies

The Chelate Timing Study was designed to determine if lead uptake could be enhanced by adding EDTA when water use by white mustard was at a maximum during bolting and flowering. The results indicated that EDTA may be applied throughout the bolting and flowering period with no effect on lead uptake by white mustard.

The Harvest Timing Study was designed to determine the time required for maximum lead accumulation by white mustard after EDTA has been added to the soil. Lead uptake increased significantly up to 48 hours after EDTA application and increased very slowly thereafter. Therefore, it is recommended that white mustard be harvested 48 hours after an EDTA application to minimize wind dispersion and shattering of senesced plants.

6.3 Recommendations for Future Work

As observed during the Soil Leaching Study, the presence of residual amounts of EDTA tends to place stress on a succeeding crop (white mustard). Consequently, future efforts should be directed towards enhancing plant growth in subsequent crops and minimizing the potential effects of EDTA. Specific areas to explore include:

- Examining use of alternate farming techniques to encourage the microbial breakdown of residual chelates (particularly after application and prior to replanting)
- Examining the application of less phytotoxic amounts of chelate
- Determining the phytotoxicity of alternate chelates

- Examining the use of multiple chelates to obtain synergistic affects for lead uptake
- Screening plants for their ability to germinate and grow in the presence of residual amounts of chelate
- Examining the use of alternate farming techniques as a means of increasing soil permeability in the root zone
- Examining the use of soil heating as a means of increasing lead uptake in the root zone
- Intercropping to maximize root exploration
- Examining the use of plant hormones to promote lead uptake and enhance plant health

While research in these areas can be conducted in laboratory and greenhouse studies, field demonstrations are needed to realistically assess the effectiveness of phytoextraction procedures for *in situ* remediation of contaminated soil.

Overall, the test results appear sufficiently encouraging to warrant field demonstration of the phytoextraction methodologies developed in the studies described in this document.

6.4 Summary

During this project, TVA tested treatment effectiveness on two moderately contaminated soils (2,500-3,500 ppm lead) which differed in chemical and physical properties (a silty clay - pH 7.0 and a silt loam - pH 7.3) which were obtained from the SFAAP. The primary project goals were to:

- Determine which of three chelates (CDTA, EDTA, or EGTA) would be the most effective at solubilizing soil lead.
- Determine the optimal chelate concentration and soil pH to use during treatment.
- Determine the best method for applying the selected chelates.
- Determine the lead uptake efficiency of cool and warm season plants species (Indian mustard, white mustard, alfalfa, corn, sorghum sudan grass, and sunflower).
- Determine if foliarly applied phosphate would enhance plant growth or decrease lead toxicity to the selected crops.
- Appraise chelate persistence and movement in soil.

- Determine the extent of lead movement in soil due to solubilization by treatments.

During the course of the project, TVA determined that the optimum treatment parameters for the SFAAP soils were:

- An application of EDTA at a one-to-one molar ratio to the lead concentration in the soil
- Use of corn as the warm season crop
- Use of white mustard as the cool season crop
- Acidification of soil to pH 5.5 in combination with EDTA when corn is the phytoextraction crop
- No soil acidification with use of EDTA when white mustard is the phytoextraction crop
- A 1 percent foliar phosphate spray may be used for corn to provide supplemental phosphorus
- No foliar phosphate application for white mustard
- Application of chelate in a volume of water to bring only the top two feet of soil to field capacity

For these soil types in this study, adherence to these parameters should result in maximum lead uptake efficiency by the plants with the least environmental risk.

The project results also indicate that:

- Foliar application of phosphates to corn did not significantly affect lead uptake by corn.

- The best harvest time for corn after EDTA application and soil acidification was at plant senescence to the point of dryness, but while still at sufficient moisture content to prevent excessive leaf shatter.

- The best results for white mustard were obtained when EDTA was applied at the onset of bolting and flowering.

- Maximum lead uptake for white mustard occurred within 48 hours after EDTA application, and harvest at this point allowed ease of handling (no leaf shatter and dispersion).

- Some downward movement of solubilized lead and EDTA occurred in soil when the crops and amendments were tested in soil leaching columns. Maintaining the moisture content of the soil at or below field capacity minimized movement.

- EDTA detected below the root zone may have been complexed with cations other than lead, which limited lead solubilization below the root zone.

Overall, the project results were encouraging. Based on these results, the phytoextraction methods examined appear likely to enhance lead removal and minimize the risk of lead leaching out of the plant root zone.

Based on techniques developed in this study, the USAEC, as lead agency, with the TVA, Alliant TechSystems, and the Twin Cities Army Ammunition Plant (TCAAP) were funded by the Environmental Security Technology Certification Program to initiate a field demonstration of phytoextraction at two sites at the TCAAP, New Brighton, MN, in spring 1998. The demonstration is scheduled to run for two years. Two-0.2 acre areas of low (740 ppm or less) or moderate (1,300-8,000 ppm) levels of lead are in use with remediation crops of corn and white mustard in summer. A chelate and soil acidification are being used to enhance lead uptake by corn, whereas only the chelate is being used with white mustard. Simultaneous resource recovery of lead and disposal of plant material is accomplished by smelting the harvested crops. Intensive soil and plant sampling coupled with a leachate collection system is being used to monitor treatment effectiveness and any potential environmental effects of the technology.

SECTION 7.0

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SECTION A
PROJECT SAMPLING PLAN

A.1 Overview of Sampling Operations

Field sampling operations were performed for the following purposes:

- Characterize and map SFAAP sites for soil type and degree of heavy metal contamination via collection of multiple soil cores at various depths at two contaminated areas.

- Collection of a bulk quantity of soil from a suitable location within each SFAAP site for use in laboratory and greenhouse studies. A suitable location is defined as a site with lead contamination levels of 3,000 to 4,000 ppm in the top foot of soil.

Laboratory and greenhouse sampling operations were performed for the following purposes:

- Collection and analyses of soil samples during laboratory studies to select chelates to be used in the greenhouse studies and to optimize chelate effectiveness in solubilizing lead and other metals in soil.

- Collection and analyses of soil samples to determine chelate persistence and movement in soil.

- Collection and analyses of plant and soil samples in greenhouse studies to determine the plant species with the highest efficiency for lead removal and to determine the amounts of lead remaining in soil after plant harvest for each species studied.

- Collection and analyses of plant and soil samples in greenhouse studies to determine the effect of phosphate in ameliorating lead toxicity to plants.

- Collection and analyses of plant, soil, and leachate samples in greenhouse studies after optimization of other experimental parameters to assess the risk of lead and metals leaching after chelate additions.

A.2 Sample Collection and Laboratory Procedures

A.2.1 Soil Sampling Procedures for Initial Characterization

Initial field sampling was conducted on an explosives burning ground located at the SFAAP. Two sites were selected for soil sampling; one site was located in Cell 1 and the other in Cell 7 (Figure 2-2).

Soil sampling was performed by TVA personnel. Safety precautions and site controls used during the sampling procedure are outlined in the Health and Safety Plan. The sampling procedure, conducted by TVA personnel, was as follows:

1. Select and mark an area measuring 90 feet by 90 feet within each of Cell 1 and Cell 7.

2. Subdivide the area into thirty-six 15-foot-square grids.

3. Further subdivide each 15-foot grid into four 7.5-foot squares.

4. Take one soil core to a depth of 12 inches from each 7.5-foot square and subdivide this core by depth into two portions (0-6 and 6-12 inches). Composite cores taken from the four 7.5-foot squares, according to depth, into one sample for each depth and place it into an appropriately identified and labeled plastic bag (Ziploc™ type).

5. Package samples for shipment to ERC and transfer to TVA's greenhouses at the TVA's Analytical Laboratory in Muscle Shoals, AL, in accordance with TVA's chain of custody procedures (TVA procedure SP-0001, "Sample Chain of Custody".)

A total of 144 samples were taken (36 grids/site x 2 depths/sample core x 2 sites = 144). Upon leaving the sampling site, all TVA personnel involved in the sampling procedure underwent decontamination in accordance with the Health and Safety Plan. The soil sampling plan is provided in Appendix D-1.

The collected soil samples were air-dried by opening the plastic bag and folding down the top to permit sufficient air movement. The opened bags were placed on tables in the greenhouse and allowed to dry for one week with periodic mixing of the soil in the bag. Following this, the soil samples were analyzed for the parameters shown in Table 4-1 and by the methods shown in Table 4-22.

A.2.2 Sampling Procedures for Bulk Soil Collection and Processing

Based on the criteria of soil texture and total lead content determined by TVA, bulk quantities of soil were collected by TVA personnel from two of the sites identified in Section 5.2.1 (1,000 kg collected per site). The soil was collected by shoveling it into 55-gallon steel drums lined with a heavy-duty plastic barrel liner. Soil sampling was performed by TVA personnel. Safety precautions and site controls used during the sampling procedure are outlined in the Health and Safety Plan. The soil in each drum was labeled both for identification and for Department of Transportation (DOT) regulatory requirements for hazardous waste and shipped by best available method to the ERC greenhouse in Muscle Shoals, AL. Copies of the soil sampling and excavation plans are provided in Appendices D-1 and D-2, respectively.

Once received, each site's soil was processed for use in laboratory and greenhouse studies by passing the soil through a precleaned gasoline-powered soil shredder fitted with a one-quarter inch stainless steel screen. The soil was thoroughly mixed and twelve subsamples were taken for analysis and characterization, as described in Table 4-2 and by the methods listed in Table 4-22. The soil then was rebarreled at the existing moisture content and stored with appropriate labels until use. Safety precautions, engineering controls, and site controls were used which were consistent with the ERC's Health and Safety and Chemical Hygiene Plans. All activities, except chemical analysis, were conducted at the ERC greenhouse to minimize the possibility of contamination.

A.2.3 Soil Sampling Procedures for Laboratory Studies

For laboratory studies, an amount of soil was removed from a selected barrel, weighed, and recorded as to the amount removed, placed in an appropriately identified and labeled plastic bag (Ziploc™ type), and transported to TVA's Analytical Laboratory in accordance with TVA's

chain of custody procedures (TVA procedure SP-0001, "Sample Chain of Custody," Appendix C-1).

A.2.4 Soil Sampling Procedures for Greenhouse Studies

For a given greenhouse study, sufficient soil was taken from the appropriate barrels (located at the greenhouse), placed on a heavy plastic sheet or tarp on a concrete floor, and thoroughly mixed. Small samples were taken for moisture determination and, if necessary, the moisture content of the soil was adjusted to one-fourth to one-third of field capacity for best handling in subsequent greenhouse operations. The soil then was covered with plastic to prevent any appreciable moisture loss until used in plant screening, foliar application, and soil leaching studies.

In the Plant Screening and Foliar Application Studies, soil was sampled post-harvest. Sampling was performed by taking three full-depth cores from the pot with a standard hand soil sampler. The cores were composited to provide one soil sample from each pot. After each sampling, the core sampler was cleaned by wiping with a damp rag and dried by wiping with a Kim Wipe. The soil samples were air-dried in open Ziploc™-type plastic bags as described previously, screened through a 2.0-mm mesh stainless steel wire screen, then transported to the TVA's Analytical Laboratory for analyses in accordance with TVA's chain of custody procedures (TVA procedure SP-0001, "Sample Chain of Custody," Appendix C-1).

In the Soil Leaching Study, soil samples were taken both pre- and post-harvest. Pre-harvest samples were taken immediately prior to soil amendment additions by removing two full-depth cores from each container. After sampling, the core sampler was cleaned by wiping with a damp rag and dried by wiping with a Kim Wipe. The cores were subdivided by depth (0"-6", 6"-12", 12"-18", and 18"-30") and composited into one sample for each depth. The composited samples were placed in Ziploc™-type plastic bags and transported to TVA's Analytical Laboratory for analysis. Core holes were filled with a sealed PVC tube before acidifier and chelate additions. To prevent amendment short-circuiting, the post-harvest samples were taken in similar fashion and transported to TVA's Analytical Laboratory for analysis. All samples were transported in accordance with TVA's chain of custody procedures (TVA procedure SP-0001, "Sample Chain of Custody," Appendix C-1). Core holes from

post-harvest soil sampling were filled with sealed PVC tubes and remained in place during replanting and growth of the second crop. Soil sampling conducted after the containers were replanted was conducted in the same way.

A.2.5 Plant Sampling Procedure

In the studies involving plant sampling, the total aerial portions of the plants were harvested from the pots when senescence, or death, occurs following the addition of the soil amendments. During the Soil Leaching Study, both root and shoot samples were taken pre- and post-harvest. For pre-harvest root sampling, roots were extracted as cores using a standard hand soil sampler. Roots were thoroughly washed and then rinsed in deionized water. After each sampling, the core sampler was cleaned by wiping with a damp rag and dried by wiping with a Kim Wipe. Core holes from post-harvest soil sampling were filled with sealed PVC tubes. Plant tissue from individual treatments were placed into appropriately labeled brown paper bags and oven dried for 72 hours at 55 degrees Celsius in accordance with standard methods of plant and soil analysis. The tissues were weighed for yield determinations, then ground to less than 2.0-mm particle size using a Wiley Mill equipped with stainless steel blades and screens. The dried, ground tissues were stored in glass bottles and transferred to TVA's Analytical Laboratory in accordance with TVA's chain of custody procedures (TVA procedure SP-0001, "Sample Chain of Custody," Appendix C-1). Plant materials were analyzed by the methods listed in Table 4-23.

A.2.6 Leachate Sampling Procedure for the Soil Leaching Study

During the first growth period of the Soil Leaching Study, soil leachates would have been collected from the containers when leaching occurred from the bottom of the column prior to the addition of soil amendments and every day after amendment addition. After plant harvest, the containers were replanted and the leachate was to be collected weekly from the containers when leaching occurred from the bottom of the column. When the plants reached full vegetative biomass, the experiments were concluded. The leachates collected from the plant containers was to drain in into a suitable sized plastic bottle. The amount of leachates was to be measured and recorded. The leachates were to be filtered through a Whatman #2 filter, or its equivalent and preserved with nitric acid to a pH of 2 or less. A subsample was to be placed

in a precleaned 125-ml plastic bottle and taken to TVA's Analytical Laboratory for analysis, and the leachates then were to be placed into a holding container until disposal. The plastic collection bottle was to be cleaned with a 6 molar solution of hydrochloric acid, triple rinsed with deionized water, and returned to service. Leachates collected during the preliminary laboratory studies were to be processed similarly. All samples were to be transferred to TVA's Analytical Laboratory in accordance with TVA's chain of custody procedures (TVA procedure SP-0001, "Sample Chain of Custody," Appendix C-1). The leachate was analyzed by the methods listed in Table 4-24.

A.2.7 Leachate Sampling Procedure for the Lysimeter Study

During the growth period of the Lysimeter Study, attempts were made to collect soil leachates from suction lysimeters positioned at 6", 12", 18", and 24" depths in the column. Samples were to be collected when leaching occurred. When the plants reached full vegetative biomass, the experiments were concluded. The leachates were to be collected from the lysimeters into 125 mL Erlenmeyer suction flasks. The amount of leachate was to be measured and recorded. The leachates were to be filtered through a Whatman #2 filter, or its equivalent, and acidified with nitric acid to a pH of 2 or less. A subsample was to be taken to TVA's Analytical Laboratory for analysis, and the leachates then were to be placed into a holding container until disposal. The subsample was to be placed in a precleaned 125-ml plastic bottle. The Erlenmeyer flasks were to be cleaned with a 6 molar solution of hydrochloric acid, triple rinsed with deionized water, and returned to service. Leachates collected during the preliminary laboratory studies were to be processed similarly. All samples were to be transferred to TVA's Analytical Laboratory in accordance with TVA's chain of custody procedures (TVA procedure SP-0001, "Sample Chain of Custody," Appendix C-1). The leachate was analyzed by the methods listed in Table 4-24.

A.2.8 <u>Laboratory Procedures</u>

Standard operating analytical procedures for data collected in the laboratory are provided in Appendices C-1 through C-22.

A.2.9 Sample Storage, Packaging, and Shipping

All samples shall be handled in accordance with TVA procedure SP-0001, "Sample Chain of Custody" (Appendix C-1). In addition, all leachate samples were to be filtered and preserved with nitric acid. Sufficient nitric acid was to be added to the leachate samples to lower the pH below 2.

No attempt was made to store samples or sample extracts beyond that period of time required for initial assessment and review of laboratory data.

A.2.10 Laboratory Equipment

The equipment used for analyzing samples is outlined in Table 4-25.

A.3 Sampling Documentation

Field sampling logs were produced and completed at the time of sampling to ensure dates, times, locations, and other pertinent data and conditions were recorded. Sample identification numbers were written on both the sample containers and sample log sheet for easy identification and cross-referencing. Sample identification codes or numbers were assigned in a logical manner to ensure ease in correlating between codes and sampling locations.

Appendix B
QUALITY ASSURANCE

B.1 Purpose and Scope of the Plan

The quality assurance (QA) plan outlined procedures to ensure that:

- Sufficient measurements were made to assess the effectiveness of the proposed treatment methods
- Samples taken were representative of the conditions in the experimental setup
- Samples were delivered to the laboratory for analysis without deterioration
- Samples were processed by the laboratory without deterioration prior to analysis
- Measurement techniques were sufficiently specific to measure the target compounds
- Data taken was reliable

The quality assurance plan applied to all activities, including performing experiments, sampling, and laboratory analysis of samples.

TVA's Analytical Laboratory provided analytical chemistry support for the project by performing analyses for metals and chelate (water-soluble EDTA). Metals analysis comprised the bulk of the workload, but additional analyses were performed for nutrients and organic carbon.

B.2 Project Responsibilities

Figure B-1 shows the TVA organizations providing support to the project. Responsibilities of the TVA project team were as follows:

The Program/Project Manager served in two capacities: Program Manager and Project Manager. As Program Manager he was responsible for providing guidance to the project team to ensure that the USAEC and TVA project and program goals were met. The Program Manager was also responsible for resolving any inconsistencies between USAEC and TVA mission objectives and those of the project/program.

As Project Manager he was responsible for overall direction of the project and was responsible for oversight and direction of staffing levels, process design, construction, installation, field process operations, technical reports, preparation and presentation of technical papers, and conducting briefings of USAEC personnel. The Project Manager was responsible for providing direction and executing tasks to ensure that project goals were met, reports were delivered on schedule, and that task schedules and costs were met. The Project Manager ensured that any variances were adequately explained.

Technical Manager was responsible for planning, directing, and executing the details of process design, construction, installation, experimental design, field process equipment operation, sampling, documentation, data integrity, data interpretation, technical reports, preparation and presentation of technical papers, and conducting briefings of USAEC personnel.

The Engineering Staff reported to the Project Manager and was responsible for various project management tasks including: project planning, cost estimating, scheduling, technical writing, compiling/editing of reports, and other project management tasks.

Analytical Laboratory was responsible for providing analytical measurements on samples required in the course of the project and was responsible for review of the data produced, documentation of analytical runs, and ensuring data integrity.

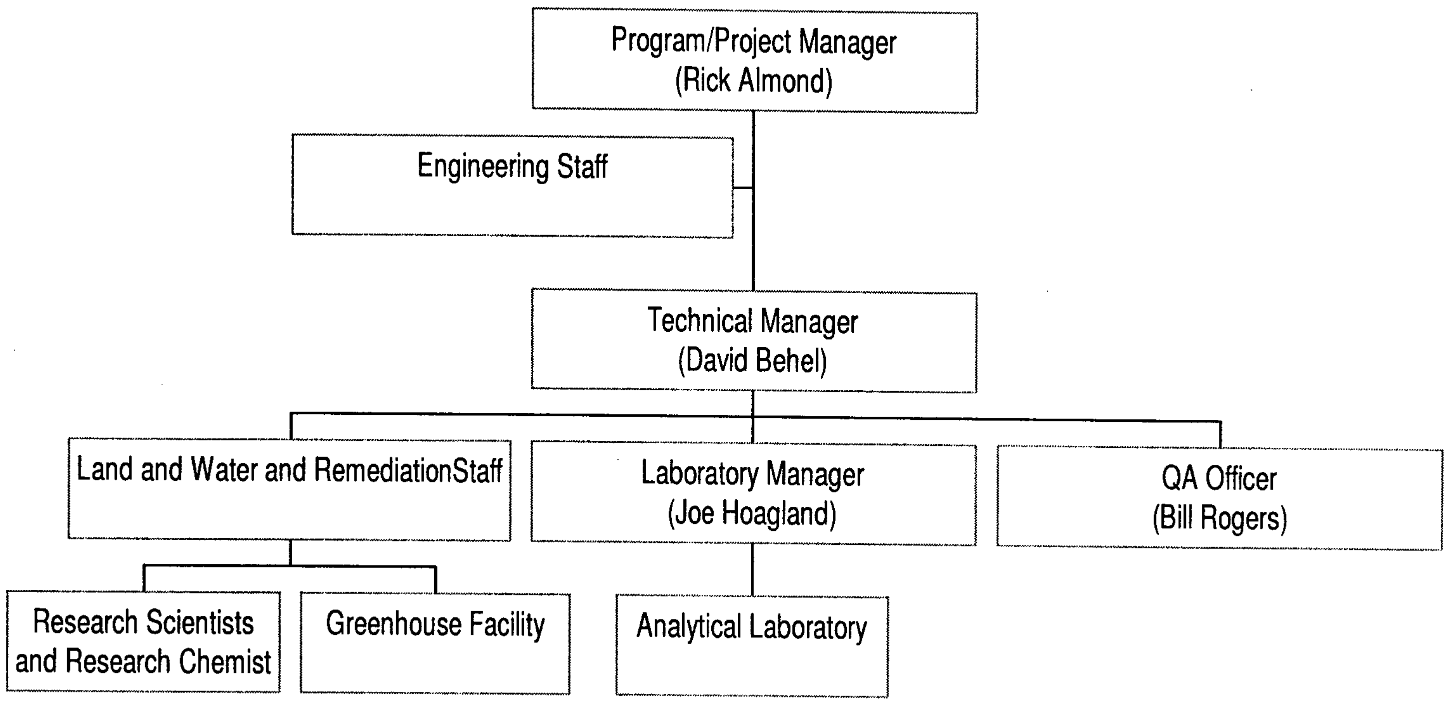

Figure B-1

TVA Organizations Providing Project Support

The Analytical Laboratory was managed by the Laboratory Manager. The Laboratory Manager reported to the Project and Technical Managers and was responsible for providing project analytical oversight and for final data integrity.

In the Analytical Laboratory, research chemists and research scientists reported to the Laboratory Manager and were responsible for planning, design, testing, and documentation of the various sub-projects assigned to them. They were responsible for producing periodic progress reports to the Laboratory Manager. They were responsible for review of data falling under their area of responsibility. Chemical laboratory analysts and technicians assigned to the Analytical Laboratory reported to the Laboratory Manager and were responsible for following procedures and instructions to provide analytical measurements required in the course of the project. They were responsible for review of the data they produced, documentation of analytical runs, and analytical equipment maintenance.

The Quality Assurance Officer was responsible for auditing actions and documentation to ensure adherence to this Plan (Section 6). The Quality Assurance Officer was responsible for providing quarterly quality control (QC) data reports to the Project Manager.

Research chemists and research scientists from Land and Water and Remediation reported to the Technical and Project Managers and were responsible for planning, design, testing, and documentation of the various sub-projects assigned to them. They were responsible for producing periodic progress reports to the Technical Manager. They were responsible for review of data falling under their area of responsibility.

The Greenhouse staff reported to the Technical Manager and were responsible for the day-to-day operations of the greenhouse and related functions.

B.3 Quality Program Procedures and Documents

B.3.1 Documenting Experimental Data

Experiments were planned in advance and documented in writing. This was done in research notebooks or separate work plans. Data, observations, experimental conditions, and changes to

plans were recorded in research notebooks in a complete enough fashion that all actions, results, and conclusions might be reconstructed afterwards. All written documents were written in ink.

B.3.2 Procedures for Field Sampling

Field sampling was conducted in accordance with written work plans, procedures, or instructions to ensure complete samples were taken at the correct locations and in a manner which did not invalidate conclusions. All field sampling actions were recorded in field notebooks or on forms designed to ensure complete documentation of all the experimental parameters.

B.3.3 Analytical Laboratory QA Manual

The analytical laboratory activities conducted during this project were conducted in accordance with the Analytical Laboratory's Quality Assurance Manual. The manual contains the following documents:

QAPLAN - "Quality Assurance Plan"
GLP-0001 - "Procedure Format and Style"
GLP-0002 - "Quality Assurance Records Control"
GLP-0003 - "Procedure Preparation and Distribution"
GLP-0004 - "Training"
GLP-0005 - "Nonconformances and Corrective Actions"
GLP-0006 - "Control of Reagents and Standards"
GLP-0007 - "Analysis Work Plan Preparation"
GLP-0012 - "Treatment of Data"
GLP-0013 - "Instrument Logbook and Control Chart Maintenance"
GLP-0016 - "Sample Receipt, Log-in, and Data Handling"
GLP-0017 - "Control of Changes to Software"
CP-0001 - "Measurement and Test Equipment Control and Calibration"
SP-0001 - "Sample Chain of Custody"

B.3.4 Procedures Policy for Analytical Laboratory Analyses

Laboratory analyses were conducted in accordance with written procedures. Three procedures were developed during the course of this project: AP-0047, "EDTA Analysis by High Performance Liquid Chromatography (HPLC)", AP-0057 "Extraction of EDTA from Soils," and AP-0064, "TKN by Flow Injection Analysis (Lachat QuikChem 8000)." The TKN procedure was written without substantive change from the manufacturer's instructions which were included as an appendix in the project plan. The EDTA procedures were developed specifically for this project from methods and approaches in open literature. The extraction procedure was carried out with deionized water. In the analytical procedure, ferric iron was added to aqueous samples or aqueous extracts which were passed through a chromatography column. The resulting iron-EDTA complex eluted as an UV-absorbing chromophore which was detected with a diode-array detector.

Analysis for metals was carried out in accordance with procedures from SW-846. However, a revision to SW-846 was promulgated since issuance of the project plan. The most recent revisions to SW-846 were followed. Other analytical techniques (cation exchange capacity, extractable lead, etc.), which consist of a specialized extraction from soil followed by a metals analysis, were carried out as proposed.

These other procedures were derived from standard EPA sources or the American Society of Agronomy.

B.4 Control of Purchased Items

Chemicals, equipment, materials, and other items purchased to conduct this project were of suitable quality to meet the project needs as specified in the written procedures. Purchased items were inspected upon receipt to ensure they met the requirements specified in purchase requests. Nonconforming items were not used. Suitable handling activities, storage conditions, and other controls were utilized to ensure quality of purchased items was not degraded after receipt.

B.5 Records

B.5.1 Record Control

Records of analysis, records of calibration, research notebooks, chromatograms, field sampling logs, custody records, work plans, machine printouts, chromatogram traces, logsheets, standard material use records, raw data calculation sheets, and copies of procedures were maintained as quality assurance records as specified in GLP-0003. Records were accumulated in logical arrangement to facilitate retention and review. In-process records and logbooks were stored in the work area in a safe manner to protect against loss, fire, spills, or other damage.

B.5.2 Record Retention

Records of experiments and analyses will be maintained for a three-year period after the end of the project. This includes machine printouts or chromatogram traces, logbooks, notebooks, logsheets, standard material use logs, and raw data calculation sheets. Due to the limited lifetime of computer storage media, any computer media utilized to store analytical file backups or raw data files will be stored for the lifetime of the project plus one year.

B.6 Performance and System Audits

B.6.1 Performance Audits

Analytical Laboratory participated in EPA Water Pollution Studies twice yearly during this project. The Analytical Laboratory investigated any analyte falling outside control limits and reported its findings to the Quality Assurance Officer in writing. Participation in this cross-checking process provides information on Analytical Laboratory's performance as compared to other laboratories in the nation. However, the cross-check spiking levels tend to be at the lower concentration ranges of the analytical techniques where relative error is large. Concentrations and matrices for the cross-check samples may not match those for the project samples, yet they are promulgated nationally and are an important part of a total quality control program, since they can provide independent information about laboratory performance that is not available from internal quality control samples.

During the project, the TVA QA Officer also introduced a purchased set of blind quality control samples and other blind quality control check samples.

B.6.2 Onsite System Audits

The TVA Quality Assurance (QA) Officer periodically inspected logs, records, printouts, results of quality control checks, documentation, case narratives, research notebooks, and other quality-related aspects of the project to ensure detailed compliance was in effect. No nonconformances were noted during this project.

B.7 Quality Assurance Reports

B.7.1 Status Reports

The Project Manager provided monthly progress reports to the USAEC. These reports contained a monthly summary of accomplishments, any significant problems encountered, problem resolution, and plans for the following month.

Quarterly quality control data reports were written by the TVA QA Officer addressing:

- Changes in this QA plan
- Changes in analytical procedures
- Summary of QC program results
- Summary of training
- Results of audits
- Results of performance sample evaluations
- Data quality assessment in terms of precision, accuracy, completeness, and MDLs
- Discussion of whether QA objectives were met

B.8 Analytical Procedures Policy

All analytical work was done in accordance with written procedures. Procedures were those promulgated by EPA, promulgated by another nationally recognized body (American Society of Agronomy), or specifically developed at TVA. No modifications to promulgated procedures were needed for the work documented in this report.

B.9 Analytical Laboratory Calibration and Quality Control

B.9.1 General Quality Control Requirements

The Analytical Laboratory ran appropriate method blanks for the procedures used in this portion of the project. Method accuracy and precision were demonstrated by running calibration checks or other quality control samples. Analysts demonstrated the ability to generate acceptable results with the methods by utilizing appropriate proficiency samples or standard reference materials. The Analytical Laboratory determined method detection limits for target compounds.

B.9.2 Batch QC

With each batch of 20 samples or subset thereof, one method blank, one matrix spike, and one laboratory control sample were run. In addition, one sample duplicate or one matrix spike duplicate was run with each batch. Note: For some analytical techniques, matrix spikes were not possible.

B.9.3 Quality Control Requirements for HPLC

HPLC was used in analysis for water-soluble (extractable) EDTA. Retention time windows were determined and the device was calibrated during development of the procedure for EDTA analysis. Five calibration standards were used.

At the beginning of each day that analyses were conducted, the midpoint calibration standard was analyzed. Then every ten samples and at the end of the run, a midpoint calibration standard was run again in accordance with the quality control requirements for HPLC devices.

B.9.4 Quality Control for Automated Laboratory Instrumentation

The quality control tests required in method 6010B were used as guidelines for the calibration and use of the equipment used in ICP methods. The quality control tests for Atomic Absorption (AA) methods for calibration and use were those specified in the 7000 series methods in SW-846.

For ICP, calibration was performed with one standard and one blank run at the beginning of each run. For AA, calibration was performed with three standards and one blank run at the beginning of each run. Following calibration, a calibration check sample and a calibration blank were run as required by the method. Typical results for calibration check samples for ICP analysis of lead are attached for two six-month periods as Figures B-2 and B-3. A small positive bias is observable in the 1998 data, but is not a major problem and would not cause rejection of any of the project data.

Flow injection analyzers (FIA) were calibrated before each use following written procedures. For FIA, calibration was performed with standards of five concentrations at the beginning of each day. Concentrations bracketed the range of interest, but were limited to the range of linear response of the device.

For each of these devices, a laboratory control sample made from a separate stock than the calibration standards was run with each batch. For any of these devices, samples exhibiting a signal above the linear range of the device were diluted and reanalyzed.

For any of these devices, a midpoint calibration standard was run at least every ten samples and at the end of the run throughout the day. Any group of ten samples preceding and following a midpoint calibration check which fell outside the 15% limits was reanalyzed.

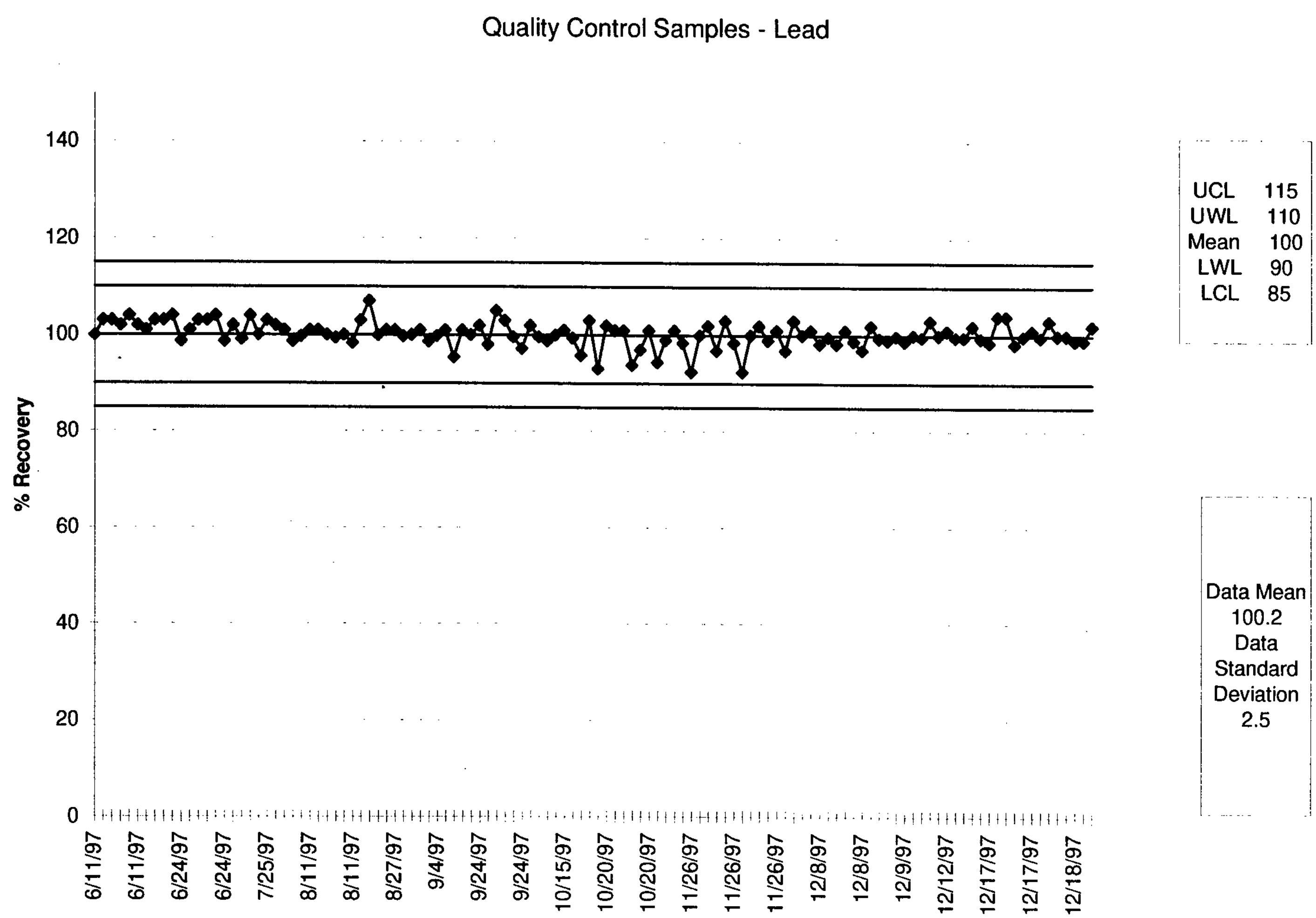

Figure B-2
1997 Quality Control Samples for Lead

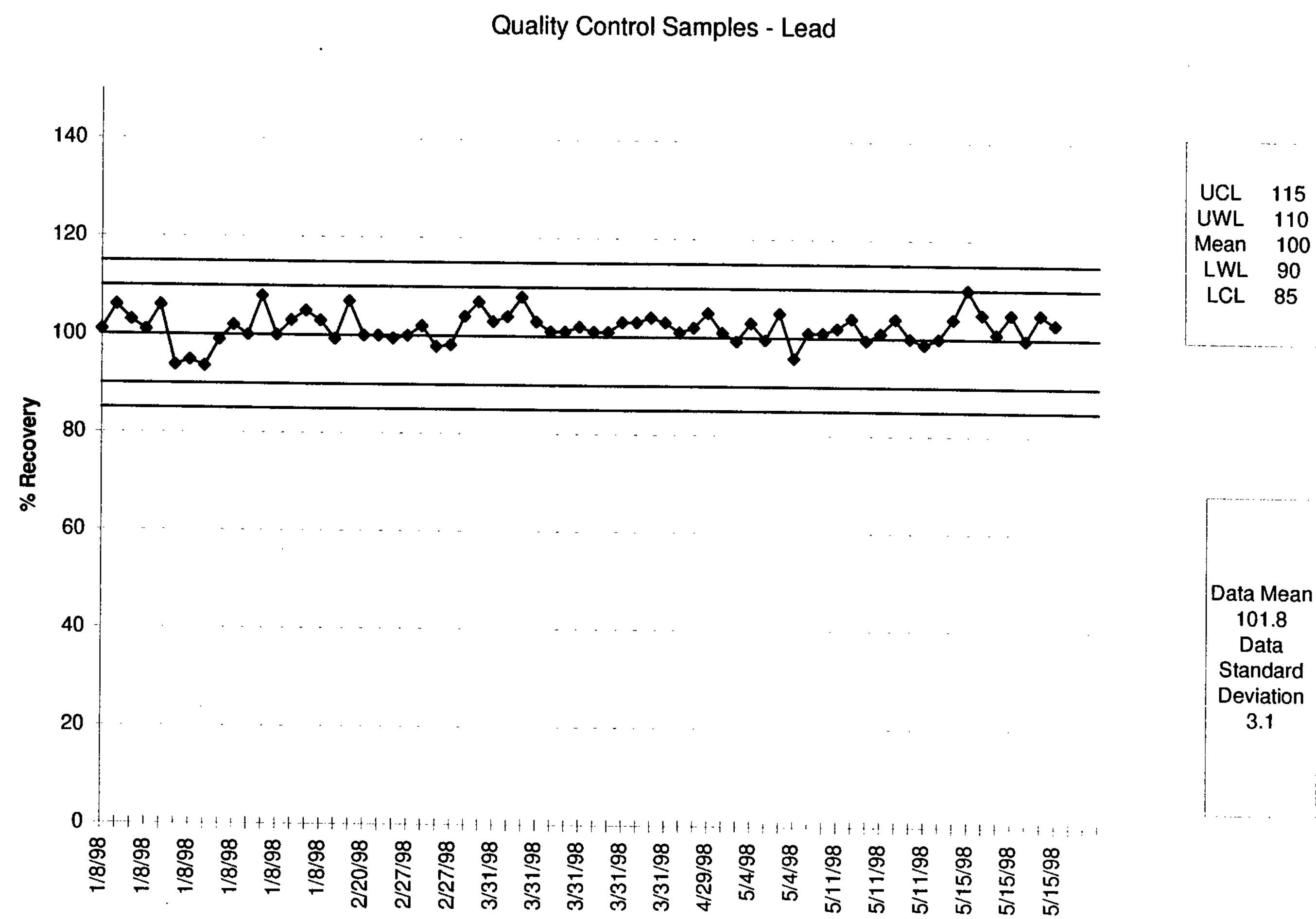

Figure B-3

1998 Quality Control Samples for Lead

B.10 Data Reduction and Validation

The project's analytical data was calculated and reduced on vendor-supplied chromatographic software for HPLC systems and on vendor-supplied analysis software for FIA systems, ICP systems, or AA systems. These systems typically calculate calibration curves automatically and apply the curves to sample measurements. However, a spreadsheet developed at TVA was used to fit curves and calculate data for the HPLC analysis. Other laboratory calculations were carried out on spreadsheets developed and tested at TVA or on hand-held calculators (e.g., soil moisture). Some devices such pH meters give direct readout or printout of analytical data.

The Analytical Laboratory's chemical Laboratory Analysts were responsible for calculation and reduction of data.

Analytical measurements were first reviewed by the chemist producing them and then by another chemist before being interfaced with the laboratory database. If quality control samples fell outside limits, the samples were usually scheduled for reanalysis. After questions were resolved, results were passed on to the Laboratory Manager for final review and validation. Group supervisors or team leaders were responsible for decisions concerning reanalysis of samples and coordinated with the Project Manager when significant problems were discovered or when resampling was required.

B.11 Equipment Logbooks

Equipment logbooks were maintained to note instrument settings, operating instructions, problems, corrections, quality control checks, and other data.

B.12 Data Reporting

B.12.1 Units

Analytical data were reported in units of milligrams per liter for liquid samples. Solid sample results were reported as milligrams per kilogram dry weight.

Method detection limits and instrument detection limits were reported for each run. Recovery of matrix spikes and recovery of quality control samples were calculated and reported as percentages.

B.13 Data Packages

Analytical data packages for the project included:

- Sample description or identification information
- Sample analytical results
- Quality control sample results with percent recovery of known compounds

Sufficient data were maintained such that every experiment and analytical result could be reconstructed.

B.14 Qualified Data

Records of all attempts at analysis were maintained whether or not the analysis was successful. However, unusable data were not reported. Data were unusable when quality control samples or quality control checks failed; however, the records for these attempts at analysis were maintained with relevant documentation. Data Qualification Codes in use by the laboratory and which may have been encountered in review of this project's data were as follows:

NA - Compound Not Analyzed

<MDL - Compound not detected (value falls less than Method Detection Limit)

TR or Trace - Compound present at trace level, indicated but less than MDL

Q - "Qualified" - For a sample in which an analyte was quantified, but `an associated quality control sample fell outside control limits

B.15 Additional QC Samples

The sampling organization submitted field blanks, field duplicates, reagent blanks, or trip blanks as instructed in the project test plan. The Analytical Laboratory counted these as samples in determining batch size.

B.16 Corrective Action

Corrective action in accordance with the requirements of GLP-0005 was not identified in the course of this project.

B.17 Data Quality Parameters for Analytical Laboratory Measurements

B.17.1 Commonly Used Quality Parameters

Percent recovery, standard deviation, relative percent difference, and other commonly used statistical indicators of accuracy were calculated as defined in Chapter 1 of SW-846, 3rd Edition.

B.17.2 Method Detection Limits and Method Quantitation Limits

Method Detection Limits were calculated as defined in Title 40, Code of Federal Regulations, Part 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit" - Revision 1.11.

Method Quantitation Limits were defined as five times the Method Detection Limit as in Chapter 1 of SW-846, 3rd Edition, or as the lowest point used in making the calibration curve, whichever was higher.

B.18 Definitions

Batch - Usually a group of no more than 20 samples of the same matrix prepared or extracted at the same time with the same reagents.

Method Blank - A sample of clean reagent carried through preparation and extraction in the same manner as samples. One method blank was run with each batch.

Matrix Spike - An aliquot of a sample spiked with a known concentration of all target analytes. Spike concentration was set to read at five times the method quantitation limit in the sample or about the midpoint of the calibration curve. One matrix spike was run for each batch.

Matrix Spike Duplicate - A second aliquot of the same sample treated in the same manner as the matrix spike.

Duplicate - A second aliquot of a sample taken independently through extraction and preparation before analysis.

Quality Control Check Sample - A quality control sample of the same type and matrix as calibration solutions, but made independently from the calibration solutions. This sample was also referred to as a laboratory control sample.

APPENDIX C

METHODS AND PROCEDURES

Appendix C-1
Lab Procedure for Chain of Custody

1.0 PURPOSE

This procedure provides instructions for sample custody from collection to final disposition.

2.0 SCOPE

This procedure applies to all samples collected under a sampling plan which requires documentation of sample custody.

3.0 SUMMARY

Requirements for documentation of sample collection and sample custody are specified.

4.0 REFERENCES

4.1 U. S. Environmental Protection Agency, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," SW-846, 3rd Edition, Most Recent Update (September 1994)

4.2 "Preparation Aids for the Development of Category II Quality Assurance Project Plans," EPA/600/8-91/004, February 1991, Guy F. Simes, Risk Reduction Engineering Laboratory, Office of Research and Developent, U.S. Environmental Protection Agency, Cincinnati, OH 45268

4.3 "Preparation Aids for the Development of Category III Quality Assurance Project Plans," EPA/600/8-91/005, February 1991, Guy F. Simes, Risk Reduction Engineering Laboratory, Office of Research and Development, U.S. Enviromental Protection Agency, Cincinnati, OH 45268

4.4 "Sample Receipt, Log-in, and Data Handling", GLP-0016, Tennessee Valley Authority, Analytical Laboratory of Environmental Applications, Muscle Shoals, AL.

5.0 RESPONSIBILITIES

5.1 The laboratory team leader shall ensure that this procedure is followed.

5.2 The sampler shall follow this procedure to ensure sample integrity in the field.

5.3 The person transporting the samples shall follow the procedure to ensure sample integrity in transit.

5.4 The person receiving the samples shall follow this procedure to ensure sample integrity upon receipt and immediately following.

5.5 Laboratory analysts shall follow this procedure during sample analysis.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Sample containers shall be cleaned to specifications of the sampling plan, or in their absence, to good commercial practice.

6.1.2 Sample containers shall have preservative added before sampling as required by the sampling plan.

6.2 Limitations and Actions

6.2.1 If the sampling organization has its own sampling procedure, sample custody procedure, labels, or custody forms, they may be substituted for the contents of this procedure as permitted by the sampling plan.

6.2.2 The number of persons handling samples from the time of sampling to receipt by the laboratory should be held to a minimum.

6.2.3 Sample containers shall be labeled by attaching tie-on tags, adhesive labels, or by writing on sample containers with indelible markers. Sample containers shall be labeled with sufficient information that they may be traced to sample collection logs, field sheets, or custody records. Choice of adhesive labels or indelible ink should take into consideration that samples may come into contact with melted ice or condensed moisture during shipment or storage.

6.2.4 Individual samples shall be sealed or sample shipping containers shall be sealed with a tamper-proof seal when they will be relinquished by TVA to a common carrier or if the sampling plan requires it. If the samples will remain in the custody of TVA employees from the time of sampling through transport to the laboratory or under lock and key (as in a locked vehicle or storage container) during this time, use of seals is not required. However, even if seals are not required, their use is strongly urged on shipping containers if the sample is to change hands several times in transport.

6.3 Requirements

6.3.1 Apparatus/Equipment

This procedure specifies no additional apparatus or equipment in addition to any sampling plan.

6.3.2 Materials

6.3.2.1 Sample containers specified in the sampling plan shall be utilized.

6.3.2.2 Labels - Samples labels shall have an adhesive which does not readily release when containers become damp.

6.3.2.3 Custody Forms - Sample chain of custody forms shall be used to record custody of samples after sampling from relinquishment by the sampling organization through transport to receipt by the laboratory. The following information shall be supplied on the custody form:

a. Project identification
b. Sample collection date
c. Sample identification
d. Collection time
e. Number of containers per sample identification code
f. Requested analysis
g. Sampling location
h. Comments
i. Signature of sample collector.

In addition the form shall contain an area so that each relinquishment and receipt of samples may be documented.

Example custody forms are attached as appendices 10.1 and 10.2. Other forms specific to a given project may be developed as long as they contain the minimum information specified above.

Note: If sample collection time and location are already recorded on a field sheet or sampling log, that information need not be repeated on this form provided a copy of the sampling information is transmitted to the laboratory with the custody sheet.

6.3.2.4 Tamper-evident seals - These seals shall be individually numbered or otherwise marked so that they could not be removed and replaced without it being detected. Two styles have been useful for samples or sample containers.

6.3.2.4.1 Adhesive seals advertised as meeting forensic science requirements, such as Kapak brand seals.

6.3.2.4.2 Padlock-style plastic seals for hasps.

6.3.2.5 Field Logbooks or Field Sheets - Sampling activities may be documented in field logbooks or field sheets designed for that purpose. When these are used, they shall contain:

a. Project identification
b. Sample collection date
c. Sample identification
d. Collection time
e. Number of containers per sample identification code
f. Reference to the sampling procedure
g. Sampling location
h. Comments
i. Signature of sample collector.

7.0 PROCEDURE

7.1 Field Operations

7.1.1 Prior to sampling, label sample containers with an adhesive label or with indelible marker. (Note: If the sampling conditions require it, labels may be affixed after sampling and cleaning the outside of the container.)

7.1.2 Document sample information in a field log, field sheet, or the custody sheet if the first two are not provided.

7.1.3 Seal the sample container with an adhesive seal if the sampling plan requires it.

7.1.4 Complete a "Sample Chain of Custody" form.

7.1.4.1 If field logs or field sheets contain collection time and location, these items may be omitted from the form. In that case, draw a diagonal line in that column and attach a copy of the field logs or sheet so that the laboratory may have pertinent sampling information.

7.1.4.2 If a numbered seal is to be used on the shipping container, note that number in the comments section of the custody form.

7.1.4.3 If the shipping container is to be sealed, sign and date the "relinquished" area of the form.

7.1.5 Place the original copy of the paperwork in a plastic bag inside the shipping container. Retain one copy for field files. Transmit a third copy by separate courier, mail or fax to the laboratory.

7.1.6 Place the samples in a shipping container. As required by the sampling plan, place ice (or commercial substitute) and a temperature test bottle in the container as well. Seal the shipping container if the sampling plan requires it. See also 6.2.4.

7.1.7 Deliver the container to be transported to the laboratory.

7.2 Laboratory Receipt (Reference also GLP-0016)

7.2.1 Inspect the seals. Open the shipping container. Inspect the sample custody form to ensure that it is correctly completed. Sign as receiver. Compare the shipping container contents to the information on the form.

7.2.2 If the "relinquished" blank is not completed and the person delivering the samples is present, have that person sign the "relinquished by." Otherwise write "Not completed", date and initial. If a person signs "relinquished by," provide that person a copy of the paperwork.

7.2.2 As required by the sampling plan, measure the temperature of any samples or temperature blanks and record that information on the custody sheet.

7.2.3 Communicate any errors, broken seals, missing seals, broken samples, differing identification numbers, extra samples, missing samples or misidentification to field personnel. Document all discussions by memorandum or database sample comment file. Document all problems and their resolution by memorandum or database sample comment file. If seals show signs of tampering, bring this to the attention of the group leader or team leader.

7.2.4 Refer to GLP-0016 for further sample receipt and log-in instructions.

7.2.6 Following logging, store the samples in a locked, refrigerated storage area as required by the sampling plan or project plan.

7.3 Laboratory Custody

7.3.1 Samples in locked storage areas, being prepared, being processed, or in autosampler trays are considered to be in the custody of the laboratory. When sampling plans require it, laboratory work areas shall be locked when unattended.

7.4 Sample Disposal

7.4.1 When customers request it, samples shall be returned to them following analysis.

7.4.2 Otherwise, dispose of samples after the time period specified in the sampling plan or project plan. If these do not specify a date, samples should be kept no longer than three months after all analyses are complete.

7.4.3 If the sampling plan requires it, document sample disposal in the workorder file, or custody records.

8.0 <u>SAFETY</u>

8.1 Wear rubber gloves and protective eyewear when handling samples unless it is known that the samples are innocuous.

8.2 Avoid contact with samples. Be aware of broken containers, corrosives, irritants, biohazards, flammability, pyrophoricity, reactivity, radioactivity

and toxicity. Inspect labels and shipping information for warnings. When hazards are known, label samples with hazard information if that is not already provided by the customer.

8.3 In case of skin contact, wash thoroughly with soap and water.

8.4 In case of eye contact, hold the eyes open and wash for at least 15 minutes in an eyewash. Call for help.

8.5 Flammable liquids must be refrigerated only in explosion-proof refrigerators to avoid the risk of explosion caused by sparks in the electrical contacts of the compressor.

8.6 In handling samples, be aware of spills on outside of containers. Clean the exterior of containers as needed.

9.0 <u>NOTES</u>

None

10.0 ATTACHMENTS AND APPENDICES

10.1 Chain of Custody Record - TVA 29203 B (RC-CTR 4-94)

CHAIN OF CUSTODY RECORD

Environmental Site Remediation • TVA Environmental Research Center • Muscle Shoals, Alabama 35660

SWMU NO.	SWMU SEQUENCE	SWMU NAME	SWMU LOCATON	PROJECT

SAMPLERS (SIGNATURE)

SAMPLE NO.	DATE	TIME	COMP/GRAB (C/G)	SAMPLE LOCATION	NO. OF CONTAINERS	ANALYTES	REMARKS

RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED BY: (SIGNATURE)	DATE/TIME	RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED BY (SIGNATURE)	DATE/TIME
RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED BY: (SIGNATURE)	DATE/TIME	RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED BY: (SIGNATURE)	DATE/TIME
RELINQUISHED BY: (SIGNATURE)	DATE/TIME	RECEIVED FOR LABORATORY BY: (SIGNATURE)	DATE/TIME	LABORATORY (NAME, CITY, STATE)			

TVA 29203 B (RG-CTR 4-94)

•COPY 1 - FIELD INVESTIGATOR •COPY 2 - FIELD INVESTIGATOR •COPY 3 - RETAINED BY LABORATORY

"Sample Chain of Custody"

10.2 Sample custody form - General

Sample Chain of Custody
Tennessee Valley Authority
Environmental Appliations CTR-1K Muscle Shoals, AL

Project

Date of Collection

	Sample ID	Collection Time*	Number of Containers	Analyses Requested	Location*	Comments
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						

	Signatures	Date and Time
Collector		
Relinquishing		
Receiving		

* These columns need not be completed if field sampling sheets containing the same information are attached

END OF PROCEDURE

Appendix C-2
Lab Procedure for Soil pH: Method ASA 12-2.6

Soil pH
ASA 12-2.6

Procedure:

1. Calibrate the pH meter according to manufacturer's instructions using two buffers to bracket the expected range of measurements. Buffers should be approximately three pH units apart.

2. Where available, check the calibration with a third buffer.

3. Prepare a slurry of soil and water in the ratio of 10.0 g to 10.0 ml.

4. Stir the slurry vigorously with a glass rod and place the electrode into the slurry. Allow the electrode to come to equilibrium and measure the pH.

5. Record information about the calibration buffers (manufacturer, expiration date, known value), the check buffer and its measurement, and sample measurements.

References:

"pH, Method 150.1 (Electrometric)," *Methods for Chemical Analysis of Water and Wastes* - Revised March 1983, U. S. Environmental Protection Agency, Cincinnati, OH, PB84-128677.

"Glass Electrode - Calomel Electrode pH Meter Method," Section 12-2.6 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

Appendix C-3
Lab Procedure for Buffer Curves

Soil Buffer Curve

An experiment in which varying amounts of acetic acid are added to soil samples. The pH is monitored over time.

1.0 Obtain the air dried percent moisture of the bulk soil you will be working with and its field capacity.

Examples: 106.0 g air dried soil/ 100 g desiccated soil and 132 g soil at field capacity per 100 g desiccated soil.

2.0 Weigh a series of eight 500g soil samples to the nearest 0.1g into plastic containers, accounting for moisture.

Example 106.0 g air dried soil/100 g desiccated soil * 500 g = 530.0 g.

3.0 Bring the soil to 55 g less than field capacity by adding the appropriate amount of deionized water to each of the eight pots.

Example: 132 g /100 g * 500 g = 660 g at capacity
660 - 530 = 130 ml water to bring it to capacity
130 - 55 = 75 ml to bring it to 55 ml less than field capacity

4.0 Add acetic acid at 0.03, 0.04, 0.05 and 0.06 milliequivalents (meq) of acetic acid per gram of soil as follows. Add the appropriate quantity of 1 N acetic acid solution (see example below) to a graduated cylinder and bring the final volume to 55 ml. Add each 55 ml solution to a pot of soil and stir well. Pour the contents of each pot onto a clean plastic sheet and work the soil to ensure mixing. Pour the contents back into the pot and

pack gently. Perform each addition in duplicate. Label each pot with the amount of acetic acid added.

Example: 1 N acetic acid = 1 meq/ml acetic acid

0.03 meq/g * 500 g /(1 meq/ml) = 15 ml 1N acetic acid

5.0 At times of 18, 24, 42, 48, and 72 hours after addition of the acid, measure the pH of an aliquot of soil as follows:

5.1 Using a stainless steel scoop, remove a portion of soil weighing approximately 30 g from the center of each of the eight pots.

5.2 Carefully repack the soil to eliminate the hole.

5.3 Slurry the soil with an equal volume of deionized water and measure the pH as in ASA 12-2.6.

6.0 References:

"Glass Electrode - Calomel Electrode pH Meter Method," Section 12-2.6 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

Appendix C-4
Lab Procedure for Cation Exchange Capacity

Exchangeable Cation Determination with Total Cation Exchange Capacity

Method ASA 9-3.1/9-4.2

Summary of Method

A soil is extracted with 1 *N* Ammonium Acetate to replace and release exchangeable cations which are then determined by metals analysis. A second extraction with 10% potassium chloride replaces and releases the ammonium ion. Ammonium ion concentration is determined colorimetrically and is equal to the Cation Exchange Capacity (CEC).

Reagents

1. 1*N* Ammonium Acetate - Dilute 1035 ml of glacial acetic acid to 14 liters with water. Add 1200 ml concentration ammonium hydroxide. Dilute to 18 liters with deionized water. Adjust to pH 7.0 with acetic acid or ammonium hydroxide. Smaller volumes may be prepared in the same ratios.

    1.1 Ammonium Hydroxide - Concentrated, reagent grade

    1.2 Acetic Acid - Glacial, reagent grade

2. 95% Ethanol - reagent grade

3. 10% KCl - Add 100g of potassium chloride to 900 ml water. Adjust to pH 2.5 with hydrochloric acid. Dilute to 1 liter with deionized water.

Procedure

ASA 9-3.1 - Exchangeable Cations - Ammonium Acetate Method

1. Sieve an air-dried soil sample through a 2 mm sieve (9 mesh).

2. Weigh 20 g of soil (< 2 mm fraction) into an extraction flask. Weigh the soil to 0.0001 g on an analytical balance. Record the weight.

3. Add 50 ml 1*N* ammonium acetate.

4. Shake for 30 minutes and allow to stand at least 6 hours, preferably overnight.

5. Swirl sample. Transfer the entire sample to a Buchner funnel fitted with Whatman #42 filter paper (or equivalent).

6. Filter, then leach the soil with 200 ml of additional ammonium acetate in four increments of 50 ml each.

Note: Do not allow the soil to dry or crack.

7. Transfer the leachate to a 250 ml volumetric flask and make to volume. Keep the soil in the funnel to determine CEC in step 9.

8. Submit the leachate for metals analysis (Na, K, Ca, Fe, etc.) for exchangeable cations by means of atomic absorption or inductively coupled plasma.

ASA 9.4.1 Cation Exchange Capacity - Potassium Chloride Method

9. Wash the soil with 200 ml of 95% ethanol in four 50 ml increments.

Note: Do not allow soil to dry or crack.

10. Using a clean suction flask, leach soil with 200 ml of 10% KCl in four 50 ml increments.

11. Transfer the leachate to a 250 ml volumetric flask and make to volume with 10% KCl.

12. Submit the leachate for ammonium analysis using a flow injection analyzer or other autoanalyzer.

13. Report results of CEC and exchangeable cations in centimole per kilogram.

$$\text{Capacity (centimoles/kg)} = \frac{X \text{ mg/L} * 0.25 * 100}{MW * WT}$$

Where X is the liquid concentration of the analyte in mg/L, WT is the weight of soil in grams and MW is the molecular weight.

Or

$$\text{Capacity (centimoles/kg)} = \frac{Y \text{ mg/kg}}{MW * 10}$$

Where Y is the concentration of the analyte in soil in mg/kg.

Analyte	MW	Factor
Na	22.99	1
Ca	40.08	2
K	39.10	1
Mg	24.31	2
Al	26.98	3
Ammonia N	14.01	1

Note: Some researchers request the capacity in centiequivalents/kg. In that case, multiply by the factor in the table above.

References

"Replacement of Exchangeable Cations, Ammonium Acetate Method" Section 9-3.1 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

"Exchangeable Acidity, Potassium Chloride Method," Section 9-4.2 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

Appendix C-5
Lab Procedure for Soil Moisture Retention/Release Curves: Method ASA 8-2.3

Water Retentivity
(Moisture Release Curves)
ASA Method 8-2.3

1.0 Procedure

Perform analysis for water retentivity (Moisture Release Curves) in accordance with ASA Method 8-2.3 as attached and in accordance with manufacturer's instructions on the Soilmoisture Model 1500 "15 Bar Ceramic Plate Extractor" as attached.

2.0 Recordkeeping

Retain all worksheets, calculations, graphs, and notes.

3.0 Quality Control Samples

The only quality control sample possible with this physical characterization method is to run a duplicate sample.

4.0 References

Chapter 8-2 "Water Retentivity." *Methods of Soil Analysis, Part I, Physical and Mineralogical Methods*, Second Edition, 1986. Arnold Klute, Editor. American Society of Agronomy, Inc. Soil Science Society of America Inc. Publisher, Madison, Wisconsin, USA.

8–2.3 Method 2[a]

8–2.3.1 SPECIAL APPARATUS

1. Membrane apparatus: Pressure-plate and pressure-membrane apparatus like those shown in Fig. 8–3 are commercially available and are usually about 28 cm. in diameter. Soil on the membrane is contained in rings of approximately 1-cm. height and 6-cm. diameter that hold about 25 g. of sample. Rubber rings must be used on acetate membranes.
2. Source of regulated air pressure: A source of compressed air at adjustable regulated pressure is required, such as that supplied by Soilmoisture Equipment Co., Santa Barbara, Calif.

8–2.3.2 PROCEDURE FOR TESTING APPARATUS

To check ceramic pressure-plate apparatus for defects, install the plates in the chamber, cover the plates with water, close the chamber, and apply the maximum appropriate air pressure. Measure the outflow rate as soon as the outflow becomes relatively free of air bubbles. Since this is a qualitative test, do not wait for a steady outflow rate. Commercial plates of approximately 28-cm. diameter, with 1- and 2-bar bubbling pressure, have a conductance of about 15 cc. $min.^{-1}$ bar^{-1}, while plates with 15-bar bubbling pressure have a conductance in the range of 0.5 to 2 cc. $min.^{-1}$ bar^{-1}. Plate conductance is not critical except for retentivity measurements at low suction values. In this case, higher conductance gives appreciably faster results.

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[a] U. S. Salinity Laboratory Staff (1954).

Next check the plates for bubbling pressure. This is the pressure difference that will cause streaming of air through a wet plate. Release the air pressure, empty excess water from the chamber, and apply the maximum air pressure to be used in the retentivity measurements. After a few minutes, the outflow of water will cease, and there should ideally be no bubbling of air. Actually a bubbling rate as high as 2 or 3 cc. of air per minute can be tolerated. Air bubbling at the outflow tube can come through the plate, but it can also come from leaks in the mounting or from joints in the outflow tube that are inside the chamber.

After observing air bubbling at the outflow tube, submerge the chamber in water, or observe air pressure change in the chamber with the supply source shut off, to make sure the chamber is air-tight. Air leaks from the chamber may produce evaporative losses that will dry the samples below the equilibrium value that would otherwise have been attained by membrane suction.

8–2.3.3 PROCEDURE FOR RETENTIVITY MEASUREMENTS

It is convenient to have 75 to 100 g. of air-dried soil. Reduce all aggregates to <2-mm. diameter by rubbing the soil through a 2-mm. round-hole sieve with a rubber stopper. Place the sieved fraction on a mixing cloth, and pull the cloth in such a way as to produce mixing. (Some pulling operations will produce segregation instead of mixing, and special care must be exercised to obtain a homogeneous sample.) Flatten the sample until the pile is 2 to 4 cm. deep.

For water retentivity, two or three representative subsamples having a fairly definite volume are required. Use a separate paper cup for each subsample. Mark with a pencil line around the inside of the cup the height of soil needed to give the desired volume of subsample. This volume should be somewhat less than the volume of soil required to make the soil-retainer ring on the membrane level full. Use a thin teaspoon or scoop (not a knife or spatula), and lift small amounts of soil from the pile. Place successive spoonfuls in successive cups, and progress around the pile until the cups are filled to the desired level. Transfer a small enough quantity of soil in each operation to keep the larger particles from rolling off the spoon or scoop. Roll-off should be avoided because it makes the extracted subsample nonrepresentative. Place the sample-retainer rings on the porous plate. To avoid particle-size segregation, dump *all* the subsample from each container into a ring, and level the soil without spilling any outside the ring. A wide-mouth powder funnel, used as a tremie, is convenient for this sample transfer operation. Allow the samples to stand at least 16 hours with an excess of water on the membrane. Close the pressure chamber, and apply pressure. Connect the outflow tube from the pressure chamber to the bottom of a 25- or 50-ml. buret.

For a pressure chamber with an acetate membrane and a rubber dia-

phragm for holding the samples against the membrane, proceed as follows: Apply the air pressure first to the soil chamber. After a short time, usually 1 or 2 hours, the water outflow rate falls off markedly. By this time, the wet samples acquire some bearing strength. Then apply an excess of pressure of about 1/4 bar to the diaphragm chamber in accordance with the manufacturer's instructions.

Samples 1-cm. high can be removed any time after 48 hours from initiating the extraction or when readings on the outflow buret indicate that liquid water outflow has ceased from all samples on each membrane. Some soils will approach equilibrium in 18 to 20 hours. Before releasing the air pressure in the chamber, put a pinch clamp on the outflow tube. This reduces backflow of water to the samples after the pressure is released. To avoid changes in the water content of the samples after opening the chamber, transfer the samples quickly to metal boxes for drying. Determine the water content by drying the samples to constant weight at 105°C. Express the water content in terms of percentage on a dry-weight basis. Retentivity data should be accompanied by information on the temperature and ambient air pressure of the soil while on the membrane. Information on the structure and history of the sample should also be given.

8–2.3.4 COMMENTS

For some purposes, the ratio R of the weight of the coarse separate (>2 mm.) to the weight of the fine separate ($\leq$2 mm.) should be recorded. Mineral soil material >2-mm. diameter complicates retentivity measurements and retains a negligible amount of water. When desired, the retentivity of the whole soil P_W can be calculated from the retentivity of the fine separate P_F by the equation, $P_W = P_F[1/(1 + R)]$.

Some air transfer always occurs through wet pressure membranes. According to Henry's law, the solubility of air in water is proportional to the pressure. Consequently, the concentration of dissolved air in the membrane water on the soil side is always higher than on the outflow side. This air moves through the membrane during liquid outflow and appears as bubbles in the outflow buret. When liquid outflow ceases, dissolved air moves through the membrane by molecular diffusion, and air bubbles will continue to appear in the outflow system, but at a reduced rate. This may amount to several cubic centimeters per minute for Visking cellulose membranes, 28 cm. in diameter, at a pressure of 15 bars. The maximum possible error from this air transfer can be calculated by assuming that all the water required to humidify these air bubbles comes from the soil samples.

The time required for soil samples to attain hydraulic equilibrium with a membrane increases approximately with the square of the height of the sample. This should be taken into consideration if it is planned to put core samples on a membrane.

Ceramic plates with rubber backing for use in pressure chambers up to

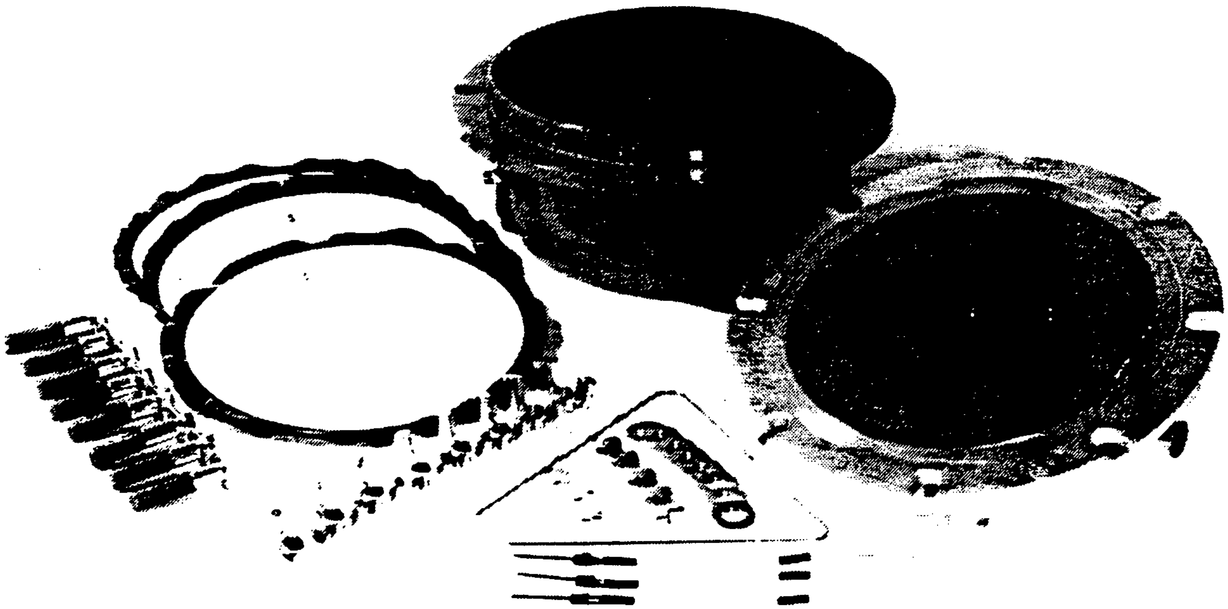
15 bars are less troublesome to use than cellulose membranes. Microbial action in some soils, iron rust from the chamber, sand grains near the gasket seal, and other things can cause disabling leaks in cellulose membranes. Pressure chambers for acetate membranes, however, do have the diaphragm for pressing the sample against the membrane to prevent loss of contact that might be caused by shrinkage of fine-textured samples.

Principal errors in retentivity measurements come from nonrepresentative subsamples: evaporative loss from samples during approach to equilibrium, as occurs on tension tables, or as caused by air leaks from pressure chambers; pressure or temperature fluctuations causing hysteresis effects: failure to attain outflow equilibrium; inadequate prewetting of samples: wetting of samples from backflow; or drying by evaporation during removal of the samples from the membrane. With skill, a coefficient of variation of 1 or 2% is attainable, and the measured value is independent of the type of apparatus or membrane.

1500

OPERATING INSTRUCTIONS

15 BAR CERAMIC PLATE EXTRACTOR



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SOILMOISTURE EQUIPMENT CORP.
P.O. Box 30025
Santa Barbara, CA 93105 U.S.A.

SOILMOISTURE

ACKING AND ASSEMBLY OF THE EXTRACTOR

REMOVE FROM BOX

THE 15 BAR CERAMIC PLATE EXTRACTOR IS SHIPPED WITH LID ASSEMBLED TO THE PRESSURE VESSEL. THE 15 BAR CERAMIC PLATE CELLS AND TRIANGULAR SUPPORT FOR BOTTOM PRESSURE PLATE CELL ARE PACKED INSIDE THE EXTRACTOR. OUTFLOW TUBE ASSEMBLIES, PLUG BOLTS AND PLASTIC SPACERS ARE PACKED SEPARATELY OUTSIDE OF THE EXTRACTOR. AFTER LIFTING UNIT FROM PACKING CRATE, SET THE EXTRACTOR DIRECTLY ON ITS FEET.

REMOVE ALL PACKING MATERIAL AND TAPE FROM AROUND CLAMPING BOLTS AND OVER OUTLET PORTS IN THE SIDE OF THE EXTRACTOR. THE PRESSURE INLET FITTING TO THE EXTRACTOR IS CAPPED WITH A THREAD PROTECTOR WHICH MUST BE REMOVED BEFORE CONNECTING HOSE IS ATTACHED.

REMOVE LID

THE EXTRACTOR LID IS READILY REMOVED BY UNDOING THE EIGHT CLAMPING BOLTS AROUND THE PERIPHERY OF THE UNIT. THE WING NUTS ON THE CLAMPING BOLTS SHOULD NOT BE COMPLETELY REMOVED. IT IS NECESSARY ONLY TO UNDO THE WING NUTS SEVERAL TURNS. THE BOLTS CAN THEN BE SLIPPED OUT OF THE SLOTS. THE BOLTS HAVE SPECIAL RECTANGULAR HEADS WHICH FIT INTO A CONSTRAINING GROOVE IN THE BOTTOM OF THE LOWER CLAMPING RING. IN REPLACING THE CLAMPING BOLTS, ALWAYS BE SURE THAT THEIR HEADS ARE PROPERLY FITTED INTO THE CONSTRAINING GROOVE.

AFTER THE CLAMPING BOLTS ARE REMOVED, THE LID CAN BE LIFTED OFF. IF THE LID ARS TO "STICK", LIFT FORCIBLY AT ONE EDGE TO BREAK CONTACT BETWEEN SEALING "O" AND LID. IT IS IMPORTANT TO HANDLE THE LID CAREFULLY SO THAT THE SEALING AREA ON THE UNDERNEATH SIDE IS NEVER SCRATCHED OR OTHERWISE DAMAGED SINCE SUCH DAMAGE WOULD PREVENT THE UNIT FROM SEALING PROPERLY. THE "O" RING ITSELF FITS INTO A GROOVE AT THE TOP EDGE OF THE PRESSURE VESSEL WALL AND IS EASILY REMOVED AND/OR REPLACED.

REMOVE PRESSURE PLATE CELLS

THE 15 BAR CERAMIC PLATE CELLS MAY NOW BE REMOVED ALONG WITH THE TRIANGULAR SUPPORT AND ALL PACKING MATERIAL. HANDLE THE CERAMIC PLATE CELLS WITH CARE TO AVOID SHARP BLOWS WHICH MAY CAUSE CRACKING OR BREAKING.

MOUNT OUTFLOW TUBE AND PLUG BOLTS

THE METAL OUTFLOW TUBE FITTING IS SHIPPED ASSEMBLED TO THE OTHER INTERNAL CONNECTING TUBES. REMOVE THE RUBBER SLEEVE FROM THE OUTFLOW TUBE FITTING BEFORE SCREWING FITTING INTO OUTLET PORT IN VESSEL WALL. SIX OUTLET PORTS ARE PROVIDED IN THE WALL OF THE VESSEL. FOUR ARE AROUND THE TOP EDGE AND TWO OTHERS ARE SPACED DOWN THE WALL OF THE VESSEL FOR USE WHEN THE THREE PRESSURE CELLS ARE BEING RUN AT THE SAME TIME. FIVE PLUG BOLTS ARE PROVIDED FOR SEALING THE UNUSED OUTLET PORTS.

THE PRESSURE SEAL AT THE OUTLET PORT IS MADE BY A SMALL NEOPRENE RUBBER "O" RING RECESSED INTO THE HEAD OF THE OUTFLOW TUBE ASSEMBLY AND PLUG BOLT. BEFORE INITIALLY INSERTING THE OUTFLOW TUBE ASSEMBLY OR PLUG BOLT, APPLY A SMALL AMOUNT OF STOPCOCK GREASE OR VASELINE ON THE EXPOSED PORTION OF THE "O" RING TO LUBRICATE IT A SLIDES AGAINST THE WALL OF THE VESSEL WHEN SCREWED INTO PLACE.

ONLY A SMALL AMOUNT OF TORQUE IS REQUIRED TO MAKE THE OUTLET PORT SEAL. A STANDARD 1/2" SIZE WRENCH WILL FIT THE OUTLET FITTINGS AND PLUG BOLTS. IN TIGHTENING

SE FITTINGS IT IS ONLY NECESSARY TO BRING THE OUTER EDGE OF THE FITTING INTO ACT WITH THE FLAT "SPOT FACED" SURFACE ON THE PRESSURE VESSEL WALL. THIS PROVIDES THE PROPER COMPRESSION ON THE "O" RING TO MAKE THE SEAL. FURTHER TIGHTENING WILL ONLY SERVE TO DAMAGE THE FITTING AND SHORTEN THE LIFE OF THE "O" RING SEAL.

MOUNT PM HINGE

IF A PM HINGE, CAT. NO. 1080, IS TO BE USED IN CONJUNCTION WITH THE EXTRACTOR IT WILL BE NECESSARY TO HAVE A CAT. NO. 1081 ADAPTER PLATE. THIS PLATE FITS ON TOP OF THE EXTRACTOR LID UNDERNEATH THE TOP CLAMP OF THE PM HINGE AND PROVIDES THE PROPER SPACING TO MATCH THE CLAMP HEIGHT. INSTRUCTIONS FOR INSTALLATION OF THE PM HINGE ARE BASICALLY THE SAME AS FOR THE PRESSURE MEMBRANE EXTRACTOR WHICH ARE INCLUDED WITH THE HINGE. IT IS USUALLY DESIRABLE TO MOUNT THE PM HINGE AT THE BACK OF THE 15 BAR CERAMIC PLATE EXTRACTOR WITH PRESSURE INLET FITTING SPACED 45° TO THE RIGHT.

CLOSING AND OPENING LID WITH PM HINGE

WHEN THE PM HINGE IS USED IT IS NECESSARY TO APPLY ADDITIONAL TORQUE ON THE TWO WING NUTS ON EITHER SIDE OF THE HINGE IN ORDER TO COMPRESS THE COUNTERBALANCING SPRING IN THE HINGE WHEN THE LID IS CLOSED. THE FOLLOWING PROCEDURE SHOULD BE ADHERED TO FOR MAXIMUM EASE AND EFFICIENCY OF OPERATION. FIRST APPLY A THIN COAT OF HEAVY GREASE (SUCH AS WHEEL BEARING GREASE--OBTAINABLE AT ANY GASOLINE SERVICE STATION) ON THE UNDERSIDE OF EACH WING NUT AND TOP OF EACH WASHER. WHEN THE LID IS CLOSED INSERT FIRST TWO CLAMPING BOLT ASSEMBLIES, ONE ON EITHER SIDE OF THE HINGE AND IMMEDIATELY ACENT TO IT. TIGHTEN FIRST ONE WING NUT UNTIL IT IS SNUG AND THEN TIGHTEN THE R ONE UNTIL SNUG. WORK BACK AND FORTH TIGHTENING FIRST ONE AND THEN THE OTHER UNTIL THE LID IS DOWN AGAINST THE TOP OF THE EXTRACTOR VESSEL. NOW INSERT THE SIX REMAINING CLAMPING BOLT ASSEMBLIES AND TIGHTEN ALL WING NUTS UNTIL THEY ARE FIRM.

WHEN THE EXTRACTOR IS BEING OPENED AFTER A RUN THE PROCESS IS JUST REVERSED. FIRST, LOOSEN AND REMOVE ALL CLAMPING BOLT ASSEMBLIES EXCEPT THE TWO ON EITHER SIDE OF THE HINGE. THEN LOOSEN ONE OF THESE REMAINING BOLTS ABOUT 1/8 TURN INITIALLY, AND THEN LOOSEN THE OTHER ABOUT 1/8 TURN. WORK BACK AND FORTH SLIGHTLY LOOSENING FIRST ONE AND THEN THE OTHER UNTIL THEY TURN EASILY (AFTER ABOUT 2-3 FULL TURNS), AND CAN BE REMOVED.

PLACEMENT OF TRIANGULAR SUPPORT

THE TRIANGULAR SUPPORT MUST BE PLACED IN THE EXTRACTOR VESSEL ON THE BOTTOM BEFORE ANY PRESSURE PLATE CELLS ARE INSTALLED. THE PURPOSE OF THE TRIANGULAR SUPPORT IS TO KEEP THE LOWER PRESSURE PLATE CELL OFF OF THE BOTTOM OF THE EXTRACTOR. THIS IS NECESSARY BECAUSE UNDER CERTAIN CIRCUMSTANCES IF IT IS NOT USED A SEAL CAN BE MADE BETWEEN THE OUTER EDGE OF THE RUBBER BACKING ON THE PRESSURE PLATE CELL AND THE FLAT BOTTOM OF THE EXTRACTOR. UNDER THESE CIRCUMSTANCES WHEN THE AIR PRESSURE IS APPLIED A LARGE PRESSURE DIFFERENTIAL WILL DEVELOP BETWEEN THE TOP AND BOTTOM OF THIS CERAMIC PLATE AND BREAK IT. BE SURE THE TRIANGULAR SUPPORT IS ALWAYS IN THE BOTTOM OF THE EXTRACTOR BEFORE THE PRESSURE PLATE CELLS ARE INSTALLED.

INSTALLING THE PRESSURE PLATE CELLS

THE FIRST PRESSURE PLATE CELL IS PLACED DIRECTLY ON THE TRIANGULAR SUPPORT AT THE M OF THE EXTRACTOR AND CONNECTION IS MADE THROUGH THE LOWEST OUTLET PORT. THE SECOND PRESSURE PLATE CELL IS SET ON THREE PLASTIC SPACERS WHICH ARE PLACED ON THE

IRST CERAMIC PLATE CELL NEAR THE OUTER EDGE AND LOCATED ABOUT 120° FROM EACH OTHER. ONNECTION TO THIS CELL IS MADE THROUGH THE MIDDLE OUTLET PORT. THE THIRD CELL IS MOUNTED SIMILARLY TO THE SECOND AND CONNECTION IS MADE THROUGH ONE OF THE OUTLET PORTS AT THE UPPER EDGE OF THE VESSEL WALL.

THE FLEXIBLE OUTER EDGE OF THE RUBBER DIAPHRAGM MAY BE USED TO LIFT THE PRESSURE PLATE CELLS IN AND OUT OF THE EXTRACTOR.

TUBE CONNECTIONS TO CERAMIC PLATE CELLS

THE CERAMIC PLATES IN GENERAL ARE NOT FLAT, AND HAVE A TENDENCY TO BE CONVEX. FOR THIS REASON IT IS NECESSARY TO SUPPORT THE PLATE WITH THE FINGERS DIRECTLY BEHIND THE OUTLET STEM WHEN THE RUBBER SLEEVE CONNECTION IS MADE. IN MAKING THE INTERNAL TUBE CONNECTIONS AT THE CELL AND AT THE OUTLET PORT, BE SURE THAT THE HARD NYLON TUBING RUNS THROUGH THE SLEEVE AND UP TO OR INTO THE METAL CONNECTING PARTS. THE NYLON TUBING WILL WITHSTAND THE HIGH EXTRACTION PRESSURES WITHOUT COLLAPSING WHEREAS THE RUBBER SLEEVES MAY NOT. IF THESE CONNECTIONS ARE NOT MADE IN SUCH A WAY THAT THE TUBING CANNOT COLLAPSE, AN ERRONEOUS EQUILIBRIUM READING WILL RESULT. THE ONLY OUTWARD EVIDENCE OF THIS MALFUNCTION WILL BE A RUSH OF AIR FROM THE OUTFLOW TUBE WHEN THE PRESSURE IN THE CHAMBER IS RELEASED, AS IS DONE AT THE END OF A RUN.

PRESSURE CONNECTION

THE SINGLE PRESSURE INLET TO THE EXTRACTOR IS A STANDARD 50/20 ADAPTER LOCATED PART WAY UP THE WALL OF THE VESSEL AND OPPOSITE TO THE OUTLET PORTS. A STANDARD T. NO. 1091 CONNECTING HOSE WILL COUPLE DIRECTLY TO THIS FITTING. THREAD SIZE OF THE SSURE FITTING IS 9/16-18. THE PRESSURE SEAL AT THE HOSE CONNECTION IS MADE WHEN THE UND "NOSE" OF THE BRASS STEM INSIDE THE HOSE NUT IS PRESSED AGAINST THE RECESSED CONICAL SURFACE OF THE 50/20 ADAPTER. THIS IS A METAL TO METAL SEAL AND IS VERY EFFECTIVE. THE SCREW THREADS ON THE FITTING AND NUT ONLY SERVE AS A MEANS OF HOLDING THE PARTS IN CONTACT. THE THREADS THEMSELVES DO NOT MAKE A SEAL. ONLY A SMALL AMOUNT OF TORQUE IS REQUIRED AND SHOULD BE USED IN CONNECTING THE HOSE.

HANDLING AND CARE OF THE 15 BAR CERAMIC PLATE CELLS AND EXTRACTOR VESSEL

CONSTRUCTION OF PRESSURE PLATE CELL

EACH PRESSURE PLATE CELL CONSISTS OF A 15 BAR CERAMIC PLATE APPROXIMATELY 10-1/4" IN DIAMETER WHICH IS SEALED ON ONE SIDE BY A THIN NEOPRENE DIAPHRAGM. AN INTERNAL SCREEN KEEPS THE DIAPHRAGM FROM CLOSE CONTACT WITH THE PLATE AND PROVIDES A PASSAGE FOR FLOW OF WATER. AN OUTLET STEM RUNNING THROUGH THE CERAMIC PLATE CONNECTS THIS PASSAGE TO THE OUTFLOW TUBE ASSEMBLY.

THE 15 BAR CERAMIC IS QUITE STRONG, HOWEVER, CARE SHOULD BE TAKEN TO AVOID SHARP BLOWS. IT IS ALSO IMPORTANT TO AVOID LARGE MECHANICAL LOADING.

CHECK OUT OF PRESSURE CELLS

BEFORE MAKING A RUN IT IS DESIRABLE TO CHECK OUT THE PRESSURE PLATE CELLS TO ACQUAINT THE OPERATOR WITH THEIR CHARACTERISTICS AND TO DETERMINE THAT THEY HAVE NOT BEEN DAMAGED IN SHIPMENT. PRIOR TO SHIPMENT EACH CELL IS TESTED FOR WATER OUTFLOW R AND AIR DIFFUSION RATE AND A PERMANENT RECORD IS MADE FOR EACH CELL.

IN MAKING THIS TEST THE GENERAL PROCEDURES AS GIVEN IN "MAKING A RUN FOR MOISTURE RETENTION STUDIES" (SEE PAGE 6) SHOULD BE FOLLOWED WITH THE EXCEPTION THAT ONLY WATER

BE USED. LET AN EXCESS OF WATER STAND ON THE SURFACE OF THE CERAMIC PLATE CELLS SEVERAL HOURS TO THOROUGHLY WET THE PLATE. APPROXIMATELY 150 ML OF WATER WILL BE REQUIRED TO FILL THE PORES OF EACH PLATE. NEXT MOUNT ONE OR MORE OF THE WETTED PLATES IN THE EXTRACTOR AND MAKE THE OUTFLOW CONNECTIONS. CAREFULLY ADD WATER ON TO THE SURFACE OF EACH CELL SO THAT THE SURFACE IS COMPLETELY COVERED TO THE MAXIMUM DEPTH PERMITTED BY THE OUTER EDGE OF THE NEOPRENE DIAPHRAM. CLOSE THE EXTRACTOR AND BUILD UP THE PRESSURE TO 15 BARS (220 PSI). AS THE PRESSURE BUILDS UP INSIDE THE EXTRACTOR THERE WILL BE A RUSH OF AIR FROM THE OUTFLOW TUBES. THIS IS CAUSED BY THE REDUCTION OF THE INTERNAL VOLUME OF THE CELL AS THE DIAPHRAGM AND SCREEN COLLAPSE UNDER THE PRESSURE IN THE EXTRACTOR. IF THE INTERNAL OUTFLOW TUBING CONNECTIONS ARE "TIGHT" AND THE CELL HAS NOT BEEN CRACKED OR DAMAGED, THIS AIR FLOW WILL STOP AFTER SEVERAL MINUTES AND THERE WILL BE A STEADY FLOW OF WATER. SMALL BUBBLES OF AIR WILL COME OUT IN THE FLOW OF WATER AT REASONABLY REGULAR INTERVALS. THIS IS AIR WHICH IS SLOWLY DIFFUSING THROUGH THE CERAMIC PLATE, AND IS TO BE EXPECTED. THE OUTFLOW RATE IN ML/MIN SHOULD BE MEASURED SOON AFTER FLOW STARTS, WHILE THE ENTIRE SURFACE OF THE CERAMIC IS COVERED WITH WATER.

AFTER A PERIOD OF TIME ALL OF THE WATER ON THE CERAMIC PLATE WILL HAVE BEEN CONDUCTED THROUGH AND FLOW OF WATER WILL STOP. THE SLOWLY DIFFUSING AIR WILL GRADUALLY CONDUCT SMALL AMOUNTS OF WATER SURROUNDING THE INTERNAL SCREEN TO THE OUTSIDE.

TO MEASURE THE RATE OF DIFFUSION A SHORT LENGTH OF RUBBER TUBING CAN BE CONNECTED TO THE OUTFLOW TUBE AND THE END INSERTED UNDER AN INVERTED GRADUATE WHICH HAS BEEN PREVIOUSLY FILLED WITH WATER. THE FLOW RATE OF THE AIR SHOULD BE LESS THAN 1/10 ML OF AIR AT ATMOSPHEREIC PRESSURE PER MIN WITH THE EXTRACTOR PRESSURE AT 220 PSI. IF THE FLOW RATE OF AIR IS APPRECIABLY HIGHER THAN THIS, IT INDICATES THAT THERE IS A LEAK IN TUBING CONNECTION OR THAT THE CELL IS CRACKED OR NOT SEALED PROPERLY.

<u>DRYING CELL AFTER RUN</u>

WHEN A PRESSURE CELL IS TO BE DRIED FOR STORAGE AFTER A RUN, IT IS IMPORTANT TO KEEP EVAPORATION DEPOSITS ON THE SURFACE TO A MINIMUM. THIS IS EASILY ACCOMPLISHED BY COVERING THE SURFACE OF THE CERAMIC PLATE WITH A THIN LAYER OF FINE DRY SOIL AND ALLOWING IT TO SET FOR SEVERAL DAYS UNTIL DRY. THE SOIL IS THEN REMOVED AND THE CELL IS STORED. BY THIS MEANS EVAPORATION DEPOSITS ARE FORMED ON THE SOIL PARTICLES RATHER THAN THE SURFACE OF THE CERAMIC PLATE.

<u>REMOVAL OF EVAPORATION DEPOSITS FROM PRESSURE PLATE CELL</u>

IF AFTER A PERIOD OF TIME THE FLOW RATE OF THE CELL DROPS DUE TO DEPOSITS, THESE CAN BE REMOVED. CALCIUM CARBONATE DEPOSITS ON THE SURFACE OF THE CERAMIC CAN BE REMOVED BY CAREFULLY SANDING THE SURFACE WITH A FINE OR MEDIUM GRADE OF GARNET OR SANDPAPER.

DEPOSITS IN THE PORES OF THE CERAMIC CAN BE REMOVED BY FLUSHING THROUGH THE PRESSURE PLATE CELL UNDER PRESSURE IN THE EXTRACTOR A 10% SOLUTION OF HYDROCHLORIC OR OTHER INORGANIC ACIDS. THIS SHOULD BE FOLLOWED BY SIMILAR FLUSH OF CLEAR WATER.

<u>BACTERIAL ACTION ON PRESSURE PLATE CELLS</u>

FOR MOST SOILS AND WORK BACTERIAL ACTION IN THE PRESSURE PLATE CELL DOES NOT PRESENT A PROBLEM. HOWEVER, TO MINIMIZE THIS CONDITION, THE INTERNAL SCREEN IS OF COPPER IN ORDER TO RETARD BACTERIAL ACTION.

IN THOSE CASES WHERE BACTERIAL ACTION IS OF IMPORTANCE THE PRESSURE PLATE CELLS CAN BE FLUSHED UNDER PRESSURE PERIODICALLY WITH A SOLUTION OF COPPER SULFATE OR

CURIC CHLORIDE IN THE MANNER DESCRIBED FOR REMOVAL OF EVAPORATION DEPOSITS.

CARE OF EXTRACTOR VESSEL

THE EXTRACTOR VESSEL AND TOP ARE RUGGEDLY CONSTRUCTED, WELL PLATED FOR PROTECTION AND SHOULD REQUIRE LITTLE ATTENTION.

IN HANDLING THE EXTRACTOR BE SURE TO PROTECT FROM DAMAGE THOSE AREAS WHERE THE "O" RING SEAL IS MADE. KEEP SOIL PARTICLES CLEAR OF THE "O" RING AND THE SEAT IN THE WALL OF THE PRESSURE VESSEL.

THE VESSEL IS ADDITIONALLY COATED ON THE INSIDE WITH AN ASPHALT BASE PAINT, "GILA COAT", MANUFACTURED BY THE W. P. FULLER PAINT CO. IN THE EVENT RUSTING DEVELOPS IN THE VESSEL IT CAN BE RECOATED AS NECESSARY WITH THIS OR A COMPARABLE MATERIAL.

GAS PRESSURE SOURCE, PRESSURE REGULATION, LABORATORY SETUP

PRESSURE REQUIREMENTS

THE 15 BAR CERAMIC PLATE EXTRACTOR REQUIRES A SOURCE OF REGULATED GAS PRESSURE OF 220 PSI OR MORE IN ORDER TO MAKE MOISTURE EXTRACTIONS FROM SOIL SAMPLES THROUGH THE WILTING POINT (15 BARS).

EXISTING PRESSURE SUPPLY

IF THE LABORATORY ALREADY HAS A REGULATED PRESSURE SOURCE FOR PRESSURE MEMBRANE [illegible]IPMENT, THEN THIS SAME SUPPLY CAN BE USED FOR THE 15 BAR CERAMIC PLATE EXTRACTOR. [illegible]SSURE CONNECTION FOR THE 15 BAR CERAMIC PLATE EXTRACTOR IS MADE TO THE SAME LINE THAT SUPPLIES AIR TO THE "EXTRACTION CHAMBER" ON THE PRESSURE MEMBRANE EXTRACTOR. APPROPRIATE SHUT OFF AND VENT VALVES SHOULD BE PROVIDED FOR THE NEW EXTRACTOR.

INITIAL SETUP

IF AN INITIAL SETUP IS BEING MADE FOR THE 15 BAR CERAMIC PLATE EXTRACTOR, THE PRESSURE SOURCE CAN BE EITHER A COMPRESSOR OR COMPRESSED GAS IN TANKS.

THE PM COMPRESSOR, CAT. NO. 500, PROVIDES A CONVENIENT, LOW COST PRESSURE SOURCE FOR ALL OF THE GAS PRESSURE EXTRACTORS AND CAN BE USED AS A PRESSURE SOURCE FOR THIS EXTRACTOR.

COMPRESSED NITROGEN OR AIR (2000 PSI) IN TANKS CAN BE USED; PARTICULARLY WHERE THE EXTRACTOR IS OPERATED ON A LIMITED BASIS. WHERE TANK GAS IS USED IT IS VERY IMPORTANT TO MAKE SURE THAT ALL PIPING IS LEAK FREE, SINCE A SMALL LEAK CAN WASTE A LARGE VOLUME OF GAS OVER A PERIOD OF A RUN.

THE INTERNAL VOLUME OF THE 15 BAR CERAMIC PLATE EXTRACTOR IS APPROXIMATELY 1/4 CU. FT. IF CONTINUOUS EXTRACTIONS ARE BEING MADE AT THE 15 BAR LEVEL AN AIR COMPRESSOR WILL BE DESIRABLE AS THE PRESSURE SOURCE.

PRESSURE REGULATION

THE TYPE OF PRESSURE REGULATOR REQUIRED WILL DEPEND ON THE TYPE OF PRESSURE SOURCE AND ON THE ACCURACY REQUIRED FOR THE STUDIES BEING CONDUCTED.

[illegible] ACCURACY OF REGULATION IS DEPENDENT ON THE CONSTRUCTION OF THE REGULATOR AND ALSO [illegible]VARIATIONS IN THE PRESSURE FROM THE SOURCE OF SUPPLY. WITH REGULATORS SUITABLE FOR USE WITH THIS EQUIPMENT ONE CAN EXPECT VARIATIONS IN THE SOURCE PRESSURE TO BE REFLECTED IN THE REGULATED PRESSURE IN THE RATIO OF ABOUT 1/12 to 1/25. IN OTHER WORDS, A

IGE IN THE PRESSURE FROM THE COMPRESSED AIR SOURCE OF 25 PSI WILL CHANGE THE ULATED PRESSURE BY 1 TO 2 PSI, DEPENDING ON THE MAKE OF THE REGULATOR. IN CASES WHERE EXTREME ACCURACY IS DESIRED THIS VARIATION CAN BE ELIMINATED BY THE PROCESS OF "DOUBLE REGULATION". THIS IS DONE SIMPLY BY PUTTING TWO REGULATORS IN SERIES. THE FIRST REGULATOR IS SET AT A SOMEWHAT HIGHER PRESSURE THAN THE SECOND IN ORDER TO SUPPLY REASONABLY CONSTANT PRESSURE TO THE SECOND REGULATOR. PRESSURE FROM THE SECOND REGULATOR IN TURN WILL BE VERY CONSTANT WITH SOURCE PRESSURE VARIATIONS REDUCED IN THE RATIO OF AT LEAST 1/100.

FOR ROUTINE DETERMINATIONS OF THE 15 BAR PERCENTAGE A SETUP USING A SINGLE HIGH PRESSURE REGULATOR IS ADEQUATE. AT LOWER PRESSURES IT WILL BE DESIRABLE TO MAKE USE OF A MORE SENSITIVE REGULATOR.

TO PROVIDE GOOD REGULATION THROUGHOUT THE WHOLE RANGE FROM 0 THROUGH 15 BARS TWO REGULATORS SHOULD BE USED. THE HIGH PRESSURE REGULATOR FOR THE HIGH RANGE WITH SIMPLE VALVING SO THAT THE PRESSURE FROM THE HIGH PRESSURE REGULATOR CAN BE DIVERTED TO THE LOW PRESSURE REGULATOR FOR WORK IN THE LOW RANGE, THUS MAKING USE OF THE PRINCIPLE OF "DOUBLE REGULATION" IN THE LOW PRESSURE RANGE.

WHERE COMPRESSED GAS IN TANKS IS USED AS A PRESSURE SOURCE, THE HOKE REGULATOR CAT. NO. 510B15 SERVES WELL AS THE HIGH PRESSURE REGULATOR. THIS CAN BE COUPLED WITH THE NORGREN REGULATOR CAT. NO. 20AG-X2G WITH 0-125 LB. COMPOUND SPRING FOR USE IN THE LOW PRESSURE RANGE.

WHERE A COMPRESSOR IS USED AS THE PRESSURE SOURCE, THE NORGREN REGULATOR CAT. NO. 20AG-X2G WITH 0-250 LB. SPRING CAN BE USED FOR THE HIGH PRESSURE WORK. THIS URN CAN BE COUPLED WITH THE NORGREN REGULATOR CAT. NO. 20AG-X2G WITH 0-125 LB. OUND SPRING FOR THE LOW PRESSURE WORK.

AIR FILTER USE WITH COMPRESSOR

IT IS DESIRABLE TO INSTALL AN AIR FILTER, SUCH AS NORGREN CAT. NO. 30AF-N2 AHEAD OF THE REGULATORS WHERE A COMPRESSOR IS USED AS THE PRESSURE SOURCE. THE FILTER HELPS TO KEEP SMALL DIRT PARTICLES OUT OF THE REGULATORS. WHEN THE REGULATED PRESSURE TENDS TO DRIFT APPRECIABLY FROM ITS SET VALUE IT IS USUALLY DUE TO AN IMPROPERLY SEATED VALVE IN THE REGULATOR; AND THIS IS FREQUENTLY DUE TO ACCUMULATION OF DIRT ON THE VALVE SEAT. INSTRUCTIONS FOR PROPER CARE AND MAINTENANCE OF REGULATORS ARE PROVIDED WITH THE REGULATORS.

PRESSURE GAUGE

FOR ACCURATE READOUT OF THE REGULATED PRESSURE A PRECISION PRESSURE GAUGE IS REQUIRED. THE ASHCROFT LABORATORY TEST GAUGE CAT. NO. 1082A WITH 0-300 PSI RANGE IS SUITABLE FOR USE WITH THE 15 BAR CERAMIC PLATE EXTRACTOR.

SOURCE OF PRESSURE REGULATING EQUIPMENT

PRESSURE CONTROL EQUIPMENT AND MANIFOLD FITTINGS CALLED OUT CAN BE OBTAINED THROUGH LOCAL DEALERS OR IF MORE CONVENIENT THROUGH SOILMOISTURE EQUIPMENT CO.

COMPLETE MANIFOLDS ASSEMBLED AND TESTED SUITABLE FOR USE WITH THIS EQUIPMENT CAN BE OBTAINED FROM SOILMOISTURE EQUIPMENT CO. WRITE FOR FURTHER DETAILS.

G A RUN FOR MOISTURE-RETENTION STUDIES

WORKING WITH THE 15 BAR CERAMIC PLATE EXTRACTOR, IS BASICALLY THE SAME AS WORKING

THE PRESSURE PLATE EXTRACTOR, CAT. NO. 1200.

HANDLING OF SOIL SAMPLES

PROPER HANDLING OF THE SOIL SAMPLES IS NECESSARY FOR ACCURATE, CONSISTENT RESULTS. FOR THIS, WE RECOMMEND THAT THE USER REFER TO THE PROCEDURES AS CALLED OUT IN THE AGRICULTURE HANDBOOK NO. 60 OF THE U.S. DEPARTMENT OF AGRICULTURE, DIAGNOSIS AND IMPROVEMENT OF SALINE AND ALKALI SOILS. THIS HANDBOOK COVERS DETAILED PROCEDURES FOR THE 1/10, 1/3, AND 15 BAR PERCENTAGE DETERMINATIONS, AND ON THE DEVELOPMENT OF MOISTURE-RENTENTION CURVES.

WHERE MOISTURE EQUILIBRIUM STUDIES ARE BEING RUN IT IS DESIRABLE TO KEEP SAMPLE HEIGHTS SMALL IN ORDER TO KEEP THE TIME TO REACH EQUILIBRIUM REASONABLE. THE TIME REQUIRED TO REACH EQUILIBRIUM VARIES AS THE SQUARE OF THE SAMPLE HEIGHT.

PREPARE DUPLICATE 25 GM. SAMPLES THAT HAVE BEEN PASSED THROUGH A 2 MM ROUND-HOLE SIEVE, FOR EACH SOIL TYPE TO BE RUN. PLACE SOIL SAMPLE RETAINING RINGS, CAT. NO. 1093, ON THE CERAMIC PLATE TO RECEIVE THE GROUP OF SAMPLES. EACH CERAMIC PLATE CELL WILL ACCOMODATE 12 SAMPLES WHEN RETAINED IN THESE RINGS. IN ORDER TO AVOID PARTICLE-SIZE SEGREGATION, DUMP ALL OF THE SOIL SAMPLE FROM EACH CONTAINER INTO ONE RING. POURING OUT PART OF THE SAMPLE AND LEAVING PART IN THE CONTAINER WILL GIVE A NONREPRESENTATIVE SAMPLE. LEVEL THE SAMPLES IN THE RING, COVER WITH SQUARES OF WAXED PAPER, AND ALLOW THE SAMPLES TO STAND AT LEAST 16 HOURS WITH AN EXCESS OF WATER ON THE PLATE.

IT IS DESIRABLE TO CONNECT THE NYLON TUBE AND RUBBER SLEEVE TO THE OUTLET STEM ON THE PRESSURE PLATE CELL PRIOR TO PLACING OF THE SAMPLES.

LOADING THE EXTRACTOR

WHEN THE SAMPLES ARE READY FOR THE EXTRACTOR REMOVE THE EXCESS WATER FROM THE CERAMIC PLATES WITH A PIPETTE OR SYRINGE, MOUNT THE CELLS IN THE EXTRACTOR AND CONNECT UP THE OUTFLOW TUBES. BE SURE THE TRIANGULAR SUPPORT IS IN THE BOTTOM OF THE VESSEL.

USE THE PLASTIC SPACERS TO SEPARATE THE PRESSURE PLATE CELLS. CLOSE ALL UNUSED OUTLET PORTS WITH THE PLUG BOLTS THAT ARE PROVIDED. BE SURE "O" RING IS IN PLACE, MOUNT LID, AND SCREW DOWN CLAMPING BOLTS.

CONNECTION TO A BURETTE

IT IS DESIRABLE TO PROVIDE A MEANS FOR DETERMINING WHEN EQUILIBRIUM HAS BEEN REACHED. THIS CAN BE EASILY DONE BY CONNECTING EACH OUTFLOW TUBE TO THE TIP OF A BURETTE WITH A PIECE OF SMALL DIAMETER TUBING. GAS DIFFUSING THROUGH THE CERAMIC PLATE PASSES CONTINUOUSLY IN SMALL BUBBLES THROUGH THIS SMALL OUTFLOW TUBE, AND KEEPS THE EXTRACTED LIQUID TRANSPORTED TO THE BURETTE. THE BURETTE CAN BE READ PERIODICALLY AND THE APPROACH TO EQUILIBRIUM CAN THUS BE FOLLOWED. IF THE PRESSURE IN THE EXTRACTOR IS MAINTAINED CONSTANT, NO MEASURABLE AMOUNT OF CHANGE IN THE BURETTE READING WILL BE OBSERVED OVER A PERIOD OF MANY HOURS OR DAYS AFTER EQUILIBRIUM IS ONCE ATTAINED.

TURNING ON THE PRESSURE

BUILD UP THE PRESSURE IN THE EXTRACTOR TO THE EQUILIBRIUM VALUE SOMEWHAT SLOWLY. THIS PROCEDURE WILL PERMIT YOU TO MAKE THE MOST ACCURATE SETTING ON THE EQUILIBRIUM V

AS THE PRESSURE BUILD UP INSIDE THE EXTRACTOR THERE WILL BE A RUSH OF AIR FROM THE OUTFLOW TUBES. THIS IS CAUSED BY THE REDUCTION OF THE INTERNAL VOLUME OF THE

...URE PLATE CELL AS THE DIAPHRAGM AND SCREEN COLLAPSE UNDER THE PRESSURE IN THE ...ACTOR.

IF THE RUN IS FOR DETERMINATIONS OF THE 15 BAR PERCENTAGE, THE PRESSURE IN THE EXTRACTOR IS SET AT 15 BARS OR 220 PSI.

WHERE THE PM COMPRESSOR IS USED AS AN AIR SOURCE, IT IS POSSIBLE THAT THE COMPRESSOR TANK PRESSURE WILL BE REDUCED BELOW THE REQUIRED LEVEL IF THE EXTRACTOR PRESSURE IS SET IMMEDIATELY AT 220 PSI SINCE THE VOLUME OF THE EXTRACTOR IS LARGE COMPARED WITH THE AIR STORAGE TANK. WHEN THIS OCCURS, SIMPLY TURN THE TIMER DIAL ON THE COMPRESSOR, MANUALLY, IN THE CLOCKWISE DIRECTION UNTIL THE COMPRESSOR STARTS. A SINGLE RUN CYCLE ON THE COMPRESSOR WILL BUILD THE PRESSURE UP ABOVE THE PRESSURE VALUE REQUIRED.

REMOVAL OF SAMPLES

SAMPLES MAY BE REMOVED WHEN READINGS ON THE OUTFLOW BURETTES INDICATE FLOW HAS STOPPED AND EQUILIBRIUM ATTAINED. MOST SOILS WILL APPROACH HYDRAULIC EQUILIBRIUM WITHIN 18 TO 20 HOURS.

AT THE CLOSE OF A RUN THE EXTERNAL TUBES RUNNING FROM THE OUTFLOW TUBE ASSEMBLIES SHOULD BE REMOVED OR PINCHED OFF TO PREVENT POSSIBLE BACK FLOW OF WATER WHEN THE PRESSURE IN THE EXTRACTOR IS RELEASED.

IMMEDIATELY AFTER THE PRESSURE REGULATOR IS SHUT OFF AND THE PRESSURE EXHAUSTED FROM THE EXTRACTOR, THE CLAMPING BOLTS AND LID ARE REMOVED. SAMPLES ARE TRANSFERRED TO MOISTURE BOXES AS SOON AS POSSIBLE AFTER RELEASE OF PRESSURE IN ORDER TO AVOID C...ES IN THE MOISTURE CONTENT.

ACTION OF GAS PRESSURE ON SOIL SAMPLES AND USES OF EXTRACTOR

AS SOON AS AIR PRESSURE INSIDE THE VESSEL IS RAISED ABOVE ATMOSPHERIC PRESSURE, THE HIGHER PRESSURE INSIDE THE VESSEL FORCES EXCESS WATER THROUGH THE MICROSCOPIC PORES IN THE 15 BAR CERAMIC PLATES. THE HIGH PRESSURE AIR, HOWEVER, WILL NOT FLOW THROUGH THE PORES SINCE THEY ARE FILLED WITH WATER AND THE SURFACE TENSION OF THE WATER AT THE GAS-LIQUID INTERFACE AT EACH OF THE PORES SUPPORTS THE PRESSURE MUCH THE SAME AS A FLEXIBLE RUBBER DIAPHRAGM. WHEN THE AIR PRESSURE IS INCREASED INSIDE THE EXTRACTOR THE RADIUS OF CURVATURE OF THIS INTERFACE DECREASES. HOWEVER, THE WATER FILMS WILL NOT BREAK AND LET AIR PASS THROUGHOUT THE WHOLE PRESSURE RANGE OF THE EXTRACTOR, FROM 0 TO 15 BARS.

AT ANY GIVEN AIR PRESSURE IN THE CHAMBER, SOIL MOISTURE WILL FLOW FROM AROUND EACH OF THE SOIL PARTICLES AND OUT THROUGH THE CERAMIC PLATE UNTIL SUCH TIME AS THE EFFECTIVE CURVATURE OF THE WATER FILMS THROUGHOUT THE SOIL ARE THE SAME AS AT THE PORES IN THE CERAMIC PLATE. WHEN THIS OCCURS, AN EQUILIBRIUM IS REACHED AND THE FLOW OF MOISTURE CEASES. WHEN THE AIR PRESSURE IN THE EXTRACTOR IS INCREASED, FLOW OF SOIL MOISTURE FROM THE SAMPLES STARTS AGAIN AND CONTINUES UNTIL A NEW EQUILIBRIUM IS REACHED. AT EQUILIBRIUM, THERE IS AN EXACT RELATIONSHIP BETWEEN THE AIR PRESSURE IN THE EXTRACTOR AND THE SOIL SUCTION (AND HENCE THE MOISTURE CONTENT) IN THE SAMPLES. FOR EXAMPLE, IF THE AIR PRESSURE IN THE EXTRACTOR IS MAINTAINED A 1 BAR OR ATMOSPHERE (15 PSI), THE SOIL SUCTION IN THE SAMPLES AT EQUILIBRIUM WILL BE AT 1 BAR. IF THE AIR PRESSURE IS MAINTAINED AT 15 BARS OR ATMOSPHERES (220 PSI) THE SOIL SUCTION AT EQUILIBRIUM WILL BE AT 15 BARS, WHICH IS THE APPROXIMATE WILTING POINT FOR ALL SOILS.

THE 15 BAR CERAMIC PLATE EXTRACTOR CAN BE USED FOR ALL TYPES OF STUDIES INVOLVING

ʼHE MOISTURE RELATIONSHIPS IN SOILS. ALL TYPES OF SOIL SAMPLES MAY BE USED WITH THE KCEPTION OF FINE CLAY SOILS THAT EXPERIENCE CONSIDERABLE SHRINKAGE AS MOISTURE IS EMOVED. THIS TYPE OF SOIL WILL SHRINK AWAY FROM THE CERAMIC PLATE IN 15 BAR EXTRACTIONS AND THE REDUCED FLOW AREA WILL NOT PERMIT THE SAMPLE TO REACH EQUILIBRIUM.

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FOR MOISTURE EQUILIBRIUM STUDIES THROUGHOUT THE WHOLE PLANT GROWTH RANGE FROM 0 TO 15 BARS, THE 15 BAR CERAMIC PLATE EXTRACTOR PROVIDES A NEW DIMENSION IN EASE OF HANDLING AND EFFICIENCY OF OPERATION.

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A COMPLETE STOCK OF ACCESSORIES AND REPLACEMENT PARTS FOR THE 15 BAR CERAMIC PLATE EXTRACTOR IS MAINTAINED FOR PROMPT DELIVERY. DETAILS AND PRICES ARE EITHER CARRIED IN THE CURRENT CATALOG OR MAY BE OBTAINED BY WRITING TO:

NOTICE

IT IS ADVISABLE TO ALWAYS USE THE CAT. NO. 1595, RIGHT ANGLE OUTFLOW TUBE ADAPTER, WHEN STACKING TWO OR MORE PRESSURE PLATE CELLS IN THE EXTRACTOR.

HE STEM ON THE ADAPTER IS PUSHED INTO THE HOLE IN THE RUBBER CONNECTING SLEEVE, BE RE NYLON CONNECTING TUBE IS BUTTED UP NEXT TO THE STEM. THE RUBBER SLEEVE IS USED LY TO MAKE A SEAL AND CANNOT BE RELIED UPON TO SUPPORT THE HIGH EXTRACTION PRESSURES.

THE HOLE IN THE RIGHT ANGLE ADAPTER HAS AN INTERNAL "O" RING WHICH MAKES A PRESSURE SEAL WHEN IT IS SLIPPED OVER THE OUTLET STEM FROM THE CERAMIC PLATE CELL. THESE ADAPTERS ARE EXTREMELY EASY TO CONNECT AND DISCONNECT FROM THE PRESSURE PLATE CELLS, WHEN THE CELLS ARE LOADED AND UNLOADED FROM THE EXTRACTOR. THE ADAPTERS ELIMINATE ANY POSSIBLE KINKING OF THE OUTFLOW TUBE ASSEMBLY AND HENCE PREVENT ANY PINCHING OFF OF THE OUTFLOW TUBE THAT CAN RESULT IN ERRONEOUS EQUILIBRIUM VALUES AND POSSIBLE DAMAGE OR BREAKAGE, UNDER CERTAIN CONDITIONS, TO THE PRESSURE PLATE CELLS.

NOTICE

IT IS NOT ADVISABLE TO USE THE CAT. NO. 1590, 15 BAR CERAMIC PLATE CELLS, SUPPLIED WITH THIS UNIT FOR DETERMINATION OF THE 1/10 BAR AND 1/3 BAR MOISTURE PERCENTAGES OF SOILS. DUE TO THE VERY SMALL PORE SIZE OF THE 15 BAR CERAMIC THE FLOW RATE THROUGH THE CERAMIC PLATE IS VERY LOW AT PRESSURE DIFFERENTIALS ACROSS THE PLATE OF 1/10 BAR (1.5 PSI) AND 1/3 BAR (5 PSI). THIS RESULTS IN EXTREMELY LONG EQUILIBRIUM TIMES AND EQUILIBRIUM MOISTURE CONTENT VALUES WILL TEND TO BE HIGHER THAN ACTUAL. FOR THE MEASUREMENT OF THE 1/10 BAR AND 1/3 BAR MOISTURE PERCENTAGE AS WELL AS ALL OTHER WORK IN THE 0 TO 1 BAR RANGE IT IS ADVISABLE TO USE THE CAT. NO. 1290 PRESSURE PLATE CELLS. THESE PRESSURE PLATE CELLS HAVE MUCH LARGER PORE SIZE THAN THE 15 BAR CERAMIC PLATE CELLS, AND IN THE 0 TO 1 BAR RANGE EQUILIBRIUM VALUES WILL BE REACHED MUCH FASTER. E CAT. NO. 1290 PRESSURE PLATE CELL WILL FIT INTO THE CAT. NO. 1500, 15 BAR CERAMIC ATE EXTRACTOR, AND THE SAME OUTFLOW TUBE CONNECTORS CAN ALSO BE USED WITH THESE CELLS.

INSTRUCTIONS FOR SETUP OF THE CAT. NO. 700-23 MANIFOLD

THE CAT. NO. 700-23 MANIFOLD SUPPLIED IS COMPLETELY ASSEMBLED AND TESTED AND READY FOR MOUNTING ON THE LABORATORY WALL. THE 3/4" THICK PLYWOOD BASE WHICH SUPPORTS THE VARIOUS COMPONENTS CAN BE DRILLED AT ANY CONVENIENT LOCATION FOR MOUNTING WITH WOOD SCREWS OR BOLTS IN THE LABORATORY WALL. NORMALLY, THE CAT. NO. 500-A PM COMPRESSOR IS SET ADJACENT TO THE LABORATORY BENCH AND THE PRESSURE CONTROL MANIFOLD. THE ATTACHED ENGINEERING DRAWING SHOWS A TYPICAL LABORATORY SETUP FOR THIS MANIFOLD. AS INDICATED ON THE ENGINEERING DRAWING, A CAT. NO. 710 CONNECTING HOSE COMBINATION IS USED FOR PRESSURE CONNECTION BETWEEN THE COMPRESSOR AND MANIFOLD. THIS CONNECTING HOSE COMBINATION HAS THE ELBOW FITTING WHICH SCREWS INTO THE BACK PRESSURE OUTLET ON THE COMPRESSOR TANK. THESE ARE 1/4" NPT PIPE THREADS AND A SUITABLE PIPE DOPE OR TAPE SHOULD BE USED TO MAKE A PRESSURE SEAL. A SHUT-OFF VALVE IS CONNECTED TO THIS ELBOW FITTING AND CAN BE USED FOR SHUTTING OFF THE AIR SUPPLY AT THE TANK. THE FLEXIBLE NEOPRENE HOSE THEN CONNECTS THIS SHUT-OFF VALVE WITH THE INLET FITTING ON THE MANIFOLD. THE THREAD SIZE OF THIS CONNECTING HOSE AS WELL AS THE CONNECTING HOSE USED TO CONNECT THE VARIOUS EXTRACTORS TO THE MANIFOLD IS 9/16-18. PRESSURE SEAL AT THE HOSE CONNECTION IS MADE WHEN THE ROUND "NOSE" OF THE BRASS STEM INSIDE THE HOSE NUT IS PRESSED AGAINST THE RECESSED CONICAL SURFACE OF THE PRESSURE FITTINGS. THIS IS A METAL-TO-METAL SEAL AND IS VERY EFFECTIVE. THE SCREW THREADS ON THE FITTING AND HOSE NUT ONLY SERVE AS A MEANS OF HOLDING THE PARTS IN CONTACT. THE THREADS THEMSELVES DO NOT MAKE A SEAL. ONLY A SMALL AMOUNT OF TORQUE IS REQUIRED AND SHOULD BE USED IN CONNECTING THE HOSES.

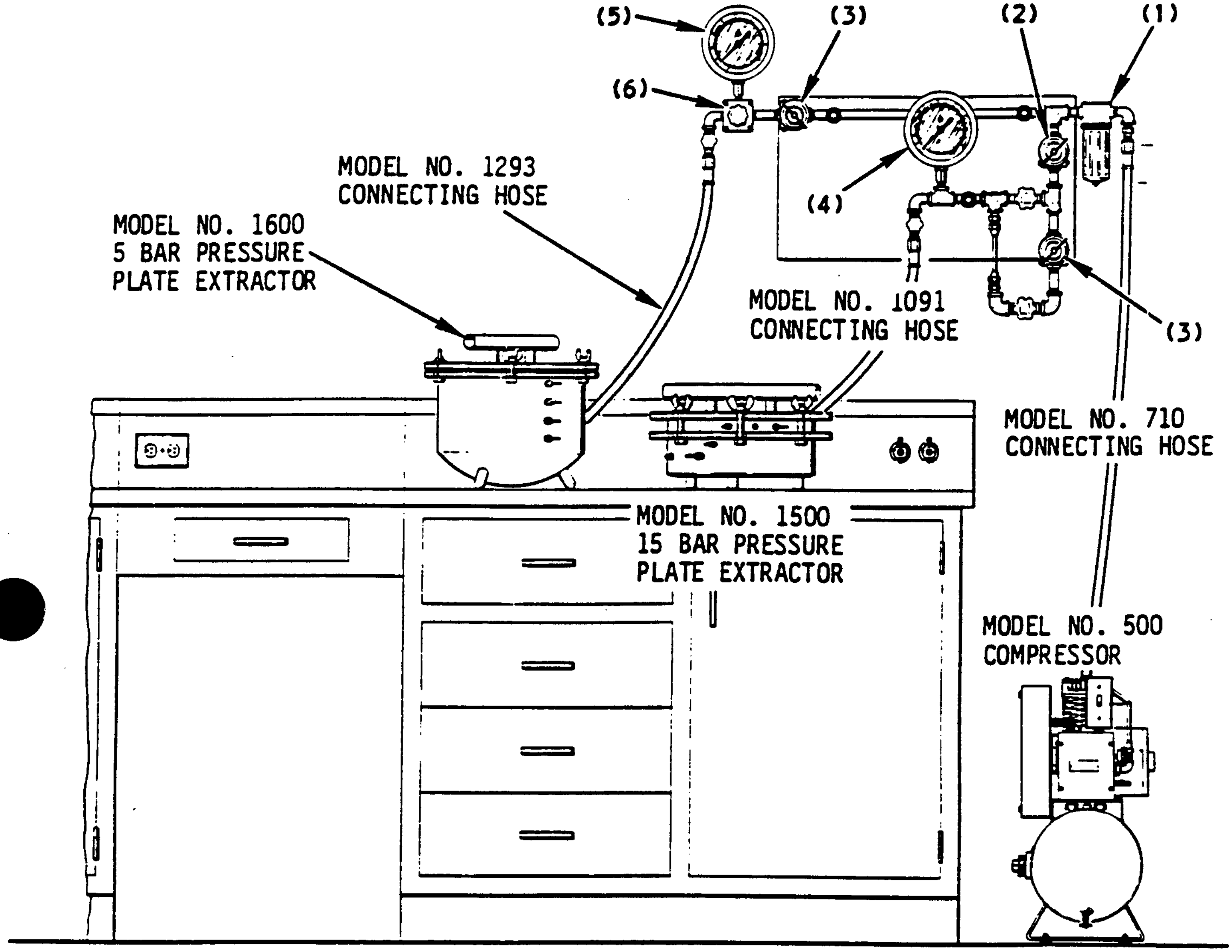
THE CAT. NO. 700-23 MANIFOLD IS A COMBINATION MANIFOLD COMBINING THE 700-2 STATION AND THE 700-3 STATION. THE 700-2 STATION IS FOR OPERATION OF THE CAT. NO. 1500 15 BAR CERAMIC PLATE EXTRACTOR. THE CAT. NO. 700-3 STATION PROVIDES VERY PRECISE LOW PRESSURE REGULATION IN THE PRESSURE RANGE FROM 0 TO 50 PSI AND IS USED FOR OPERATION OF THE CAT. NO. 1200 PRESSURE PLATE EXTRACTOR, CAT. NO. 1250 VOLUMETRIC PRESSURE PLATE EXTRACTOR, CAT. NO. 1400 AND 1450 TEMPE PRESSURE CELLS, AND THE CAT. NO. 1600 5 BAR EXTRACTOR.

THE CAT. NO. 700-2 STATION CONSISTS OF A CAT. NO. 11-002-017, 0 TO 250 PSI, PRESSURE REGULATOR; A CAT. NO. 11-002-013, 0 TO 125 PSI, PRESSURE REGULATOR; A CAT. NO. 1082-A, 0 TO 300 PSI, TEST GAUGE; AND ALL NECESSARY VALVES AND FITTINGS. IN SETTING EXTRACTION PRESSURES IN THE RANGE FROM 125 PSI TO 225 PSI, VALVE A, REFERENCE THE ATTACHED ENGINEERING DRAWING, IS OPENED, AND VALVE B IS CLOSED. ALL PRESSURE REGULATION IS THEN DONE WITH THE ONE CAT. NO. 11-002-017 REGULATOR. THE REGULATOR IS TURNED CLOCKWISE FOR HIGHER PRESSURE VALUES AND THE PRESSURE IS READ DIRECTLY ON THE TEST GAUGE. FOR LOW EXTRACTION PRESSURES IN THE RANGE FROM 0 TO 125 PSI, VALVE A IS CLOSED AND VALVE B IS OPENED. THE HIGH PRESSURE REGULATOR, CAT. NO. 11-002-017, IS SET FOR A PRESSURE VALUE IN EXCESS OF 125 PSI, AND USUALLY IN THE RANGE OF 125 TO 150 PSI. THIS HIGH PRESSURE REGULATOR THEN SUPPLIES PRESSURE TO THE 11-002-013 LOW PRESSURE REGULATOR. THIS LOW PRESSURE REGULATOR IS THEN SET FOR THE EXTRACTION PRESSURE DESIRED AND THE PRESSURE IS READ OUT ON THE TEST GAUGE.

THIS SYSTEM FOR LOW PRESSURE REGULATION IS KNOWN AS "DOUBLE REGULATION" AND IS FREQUENTLY USED TO PROVIDE VERY ACCURATE CONTROL OF PRESSURE. ALL REGULATORS REFLECT IN THEIR OUTPUT PRESSURE VARIATIONS PRESENT IN THE PRESSURE FROM THE SOURCES OF SUPPLY. BY PLACING TWO REGULATORS IN SERIES, SUCH AS MENTIONED ABOVE, VARIATIONS IN THE OUTPUT PRESSURE FROM THE FIRST REGULATOR ARE CONSIDERABLE REDUCED BY THE SECOND REGULATOR SO THAT THE OUTPUT PRESSURE FROM THE SECOND REGULATOR IS VERY CONSTANT WITH SOURCE PRESSURE VARIATIONS REDUCED IN THE RATIO OF 1:100 OR MORE.

LAB 023
LABORATORY SET-UP

700-23 MANIFOLD WITH MODEL NO. 1500 AND MODEL NO. 1600 PRESSURE EXTRACTORS



MODEL NO. 700-23 MANIFOLD, INCORPORATING:

(1) #760G1 AIR FILTER (FORMERLY #12-005-013)
(2) #766P0250 REGULATOR (FORMERLY 11-002-017)
(3) #766P0125 REGULATOR, TWO (FORMERLY 11-002-013)
(4) #780P0300 0-300 PSI TEST GAUGE (FORMERLY 1082-A)
(5) #780P0060 0-60 PSI TEST GAUGE (FORMERLY 1082-A)
(6) #765 NULLMATIC REGULATOR (FORMERLY 40-50)
ALL NECESSARY VALVES AND FITTINGS

LABORATORY SETUP FOR MODEL NO. 1500, 15 BAR CERAMIC PLATE EXTRACTOR AND MODEL NO. 1600, 5 BAR EXTRACTOR USING MODEL NO. 1290 PRESSURE PLATE CELL OR MODEL NO. 1690, 3 BAR CERAMIC PLATE CELL, OPERATING INDEPENDENTLY WITH THE MODEL NO. 500 COMPRESSOR AS A PRESSURE SOURCE.

SOILMOISTURE EQUIPMENT CORP.

P. O. Box 30025
Santa Barbara, CA 93105
U.S.A.

Telephone No. (805) 964-3525
FAX No. (805) 683-2189
Cable Address: SOILCORP

SOILMOISTURE

AT THE END OF A RUN WHEN IT IS DESIRED TO EXHAUST THE AIR FROM THE EXTRACTOR, IT IS ONLY NECESSARY TO CLOSE EITHER OF THE REGULATORS BEING USED BY TURNING IN A COUNTERCLOCKWISE DIRECTION. AS THIS IS DONE, THE AIR FROM THE EXTRACTOR WILL EXHAUST THROUGH THE REGULATOR. THIS IS A FEATURE OF "RELIEVING TYPE" REGULATORS AND IT ELIMINATES THE NECESSITY OF HAVING A SEPARATE EXHAUST VALVE. ON A RELIEVING TYPE REGULATOR, ANY PRESSURE ON THE OUTPUT SIDE OF THE REGULATOR WHICH IS IN EXCESS OF THE PRESSURE VALUE SET BY THE REGULATOR WILL AUTOMATICALLY EXHAUST THROUGH THE REGULATOR MECHANISM.

THE 700-3 STATION CONSISTS OF A CAT. NO. 11-002-013, 0 TO 125 PSI, PRESSURE REGULATOR; A NULLMATIC PRESSURE REGULATOR, 0 TO 60 PSI; CAT. NO. 1082-A, 0 TO 60 PSI TEST GAUGE; AND ALL NECESSARY VALVES AND FITTINGS. IN MAKING PRESSURE SETTINGS AT THIS STATION, IT IS IMPORTANT TO CAREFULLY ADJUST BOTH OF THE PRESSURE REGULATORS. THE NULLMATIC REGULATOR CONTINUOUSLY EXHAUSTS A CERTAIN AMOUNT OF AIR WHEN IT IS USED ON "DEAD END SERVICE" SUCH AS IS THE CASE WITH OUR EXTRACTORS. THE AMOUNT OF AIR EXHAUSTED IS PROPORTIONAL TO THE PRESSURE DIFFERENCE BETWEEN THE SUPPLY AIR AND THE PRESSURE SETTING OF THE DELIVERED AIR. FOR NORMAL USE AND FOR MAXIMUM CONSERVATION OF COMPRESSED AIR FROM THE TANK, THE CAT. NO. 11-002-013 REGULATOR SHOULD BE SET AT A PRESSURE 2-3 PSI HIGHER THAN THE EQUILIBRIUM PRESSURE THAT YOU WISH TO DELIVER FROM THE NULLMATIC REGULATOR. WHEN THIS PROCEDURE IS FOLLOWED, THE AMOUNT OF AIR ESCAPING FROM THE NULLMATIC REGULATOR IS IN THE ORDER OF 2/100 CU.FT. OF AIR PER MINUTE. THIS AMOUNT OF AIR IS VERY EASILY BUILT UP BY THE COMPRESSOR PUMP IN THE COURSE OF ITS PUMPING CYCLE.

WHEN SETTING THE PRESSURE FOR A RUN, THE PROCEDURE IS AS FOLLOWS, REFERENCE THE ATTACHED ENGINEERING SKETCH. THE VALVE AT THE END OF THE CONNECTING HOSE IS FIRST CLOSED. THE NULLMATIC REGULATOR IS THEN OPENED A NUMBER OF TURNS SO THAT YOU ARE SURE IT IS SET AT A PRESSURE CONSIDERABLY ABOVE THAT WHICH YOU PLAN TO USE. THEN, THE CAT. NO. 11-002-013 REGULATOR IS OPENED SO THAT THE PRESSURE CAN FLOW THROUGH THE NULLMATIC REGULATOR AND REGISTER ON THE TEST GAUGE. THE CAT. NO. 11-002-013 REGULATOR IS ADJUSTED SO THAT THE PRESSURE GAUGE READS, SAY, 3 PSI HIGHER THAN THE EQUILIBRIUM PRESSURE YOU PLAN TO USE IN THE EXTRACTOR. THE NULLMATIC REGULATOR IS NOW CLOSED UNTIL THE EXCESS AIR IS EXHAUSTED UP TO THE PRESSURE VALUE YOU DESIRE IN THE EXTRACTOR AND WHICH WILL NOW BE REGISTERED ON THE TEST GAUGE. THE VALVE TO THE PRESSURE EXTRACTOR CAN NOW BE OPENED AND THE REGULATORS WILL MAINTAIN THE PRESSURE IN THE EXTRACTOR AT THE VALUE SET.

IN ORDER TO EXHAUST THE AIR FROM AN EXTRACTOR AFTER A RUN, EITHER OF THE PRESSURE REGULATORS ARE SIMPLY CLOSED IN A COUNTERCLOCKWISE DIRECTION AND, SINCE THESE ARE BOTH RELIEVING TYPE REGULATORS, THE AIR FROM THE EXTRACTOR WILL EXHAUST THROUGH THE REGULATOR.

EQUIPMENT LIST WITH NORMAL ACCESSORIES:

1	1500	15 BAR CERAMIC PLATE EXTRACTOR
1	1080	PM HINGE
1	1081	ADAPTER PLATE
1	1091	CONNECTING HOSE
6	1093	SOIL SAMPLE RETAINING RINGS, per dz.
1	1600G1	5 BAR PRESSURE PLATE EXTRACTOR WITH 4 EA. MODEL NO. 1290 1 BAR PRESSURE PLATE CELLS
2	1690	3 BAR PRESSURE PLATE CELL
1	1293	CONNECTING HOSE, 40" long
1	700-23	MANIFOLD
1	710	CONNECTING HOSE COMBINATION, 60" LONG
1	500	PM COMPRESSOR - SEE ORDERING INFO BELOW

ORDERING INFORMATION:

When ordering, please specify one of the Model No.'s below

LAB 023	Laboratory Set-up less Compressor
LAB 023G1	Laboratory Set-up w/110V, 60CY. Compressor
LAB 023G2	Laboratory Set-up w/230V, 60CY. Compressor
LAB 023G3	Laboratory Set-up w/110V, 50CY. Compressor
LAB 023G4	Laboratory Set-up w/230V, 50CY. Compressor

ADDRESS ORDERS TO:

SOILMOISTURE EQUIPMENT CORP.
P.O. Box 30025
Santa Barbara, CA 93105 U.S.A.

Telephone:
Area Code 805 964-3525

Cable Address:
Soilcorp

Plant and Office Location:
801 South Kellogg Ave.
G[illegible] CA 93117

All prices are in U.S. Dollars, F.O.B. Santa Barbara, California, U.S.A. — Subject to change without notice.

On Export Orders we are prepared to handle details of export packing and forwarding and will submit Proforma Invoices covering all costs delivered, upon receipt of detailed requirements.

Appendix C-6
Lab Procedure for Soil Moisture Analysis: Method ASA 21.2.2.2

Soil Moisture, Oven Drying Method
ASA Physical Method 21-2.2.2

1.0 Purpose

To determine the moisture loss of a soil sample by oven drying overnight at 105 °C.

2.0 Scope

This procedure applies to soil, sand, silt, rock, and soil organic matter.

3.0 Summary

A sample is dried overnight at 105 °C. Moisture content is determined by weight loss.

4.0 References

Chapter 21-2.2 "Gravimetry With Oven Drying." *Methods of Soil Analysis, Part I, Physical and Mineralogical Methods*, Second Edition, 1986. Arnold Klute, Editor. American Society of Agronomy, Inc. Soil Science Society of America Inc. Publisher, Madison, Wisconsin, USA.

ASTM D 2216-92, "Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock"

ASTM D 2974-87 (Reapproved 1995) "Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils"

5.0 Responsibilities

5.1 The Laboratory Manager shall ensure that this procedure is followed during the analysis of samples.

5.2 The Laboratory Group Leader shall review and approve data produced under this procedure.

5.3 The laboratory analyst shall follow this procedure and laboratory safety guidelines. The analyst shall record all data, calculate results, and sign a written report of the analysis.

6.0 Requirements

6.1 Prerequisites

None

6.2 Limitations and Actions

For extremely dry soils, the quantity weighed should be increased in step 7.1.3 to 50g.

6.3 Requirements

6.3.1 Apparatus/Equipment

6.3.1.1 Laboratory oven with forced air, thermostatted to control temperature to plus or minus 5 °C.

6.3.1.2 Desiccator with active dessicant (Drierite, or Anhydrone)

6.3.1.3 Tongs or insulated gloves

6.3.1.4 Analytical Balance - capable of weighing to 0.0001 g.

6.3.2 Reagents and Standards

None

6.4 Quality Control Sample Requirements

Run a duplicate sample and method blank for every batch of 20 samples or subset thereof.

7.0 Procedure

7.1 Procedure Instructions

7.1.1 Thoroughly mix a portion of soil. Remove stones larger than 1 cm diameter. Remove roots and leaves. Break up any lumps or adhesions.

7.1.2 Dry a beaker or weighing dish for 30 minutes at 105 °C. Allow to cool in a desiccator with active dessicant.

7.1.3 Obtain the tare weight of the container then the weight plus 10 to 20g soil (record weight to 0.0001g).

7.1.4 Place the moist sample and container in the drying oven overnight (approximately 16 hours) at 105 °C uncovered.

7.1.5 Remove the container from the oven and place it in a desiccator with active dessicant to cool.

7.1.6 Weigh the dried sample and container.

7.2 Calculations and Recording Data

7.2.1 Calculate the water content of the material to the nearest 0.1% as follows:

$$w = [(M_{cws} - M_{cs})/(M_{cs} - M_c)]* 100$$

where

w = water content, %
M_{cws} = mass of container and wet specimen in grams
M_{cs} = mass of container and dry specimen in grams
M_c = mass of container

7.2.2 Calculate the percent solids to the nearest 0.1% as follows:

$$\text{Percent solids} = 100 - w$$

7.2.3 Record data on the form provided in 10.1.

Note: A spreadsheet may be used to calculate the data.

8.0 Safety

8.1 Follow general laboratory safety rules. Exercise care in removing hot items from the oven. Use tongs or insulated gloves.

8.2 Excercise caution to not spill hot soil containing organic matter into Anhydrone (magnesium perchlorate) which is a strong oxidizing agent.

9.0 Notes

None

10.0 Attachments and Appendices

10.1 Soil Percent Moisture Worksheet

Percent Moisture
Oven Drying Water Worksheet

Initial Date/Time ____________________ Initial Oven Temp ________
Final Date/Time ______________________ Final Oven Temp ________

Workorder						
Fraction						
Gross Wt						
Tare Wt						
Dried Wt						

Wt sample						
Wt loss						
% Moisture						
%Solid						

Entered by ______________________ Date __________

Reviewed by _____________________ Date __________

END OF PROCEDURE

Appendix C-7
Lab Procedure for Total Organic Carbon (TOC): Method ASA 29-3.5.2

Total Organic Carbon - Rapid Dichromate Oxidation Technique
ASA Method 29-3.5.2

Summary of Method

Organic carbon in soil is oxidized by reacting with potassium dichromate. The heat of dilution of sulfuric acid in water provides heat for the reaction. Excess dichromate is titrated with ferrous ion using *o*-phenthroline as the indicator. The oxidation reaction is as follows:

$$2\ Cr_2O_7^{2-} + 3\ C + 16\ H^+ = 4\ Cr^{3+} + 3\ CO_2 + 8\ H_2O$$

Reagents

1. 1 *N* Potassium Dichromate Solution. Dissolve 49.04 g of reagent-grade $K_2Cr_2O_7$ (dried at 105°C) in water, and dilute the solution to 1 liter in a volumetric flask.

2. Sulfuric Acid, concentrated (not less than 96%). If chloride is present in soil, add silver sulfate at 15g/l.

3. *o*-Phenanthroline-ferrous complex, 0.025M. Dissolve 14.85 g of *o*-phenanthroline monohydrate and 6.95 g of ferrous sulfate heptahydrate in water. Dilute the solution to a volume of 1,000ml. (This complex is also available under the trade name of Ferroin.)

4. 0.5 *N* Ferrous Sulfate solution. Dissolve 140 g of reagent-grade $FeSO_4$•7H2O in water. Add 15 ml concentrated sulfuric acid. Cool the solution and dilute it to a volume of 1,000ml. Standardize this reagent daily by titrating against 10.0 ml of 1N potassium dichromate.

Or

0.5 *N* Ferrous Ammonium Sulfate Solution. Dissolve 196 g of reagent-grade $(NH_4)_2SO_4$•FeSO4•6H2O in water. and dilute it to a volume of 1,000ml. Standardize this reagent daily by titrating against 10.0 ml of 1N potassium dichromate.

Procedure

1. Grind the soil to pass through a 0.5-mm sieve, avoiding iron or steel mortars.

2. Transfer a weighed sample, containing 10 to 25 mg of organic C, but not in excess of 10g of soil, into a 500-ml wide-mouth flask.

3. Add 10 ml of 1N $K_2Cr_2O_7$ with a volumetric pipette. Swirl the flask gently to disperse the soil in the solution.

4. Rapidly add 20 ml concentrated sulfuric acid, directing the stream into the suspension. Immediately swirl the flask gently until soil and reagents are mixed, then more vigorously for a total of 1 minute.

5. Allow the flask to stand on a heat-impervious surface for about 30 minutes.

6. Add 200 ml water to the flask, and filter the suspension if experience with the particular soil shows that the endpoint of the titration cannot be otherwise be clearly discerned.

7. Add three drops o-phenanthroline indicator and tirate the solution with 0.5N $FeSO_4$. As the endpoint is approached, the solution takes on a greenish cast and then changes to a dark green. At this point, add the ferrous sulfate solution drop by drop until the color changes sharply to blue to red (maroon in reflected light against a white background.)

8. To standardize the dichromate, make a blank determination without soil.

9. Repeat the determination with less soil if greater than 75% of the dichromate is reduced.

10. Calculate the results as follows:

$$\text{Organic C \%} = (\text{meq } K_2Cr_2O_7 - \text{meq } FeSO_4)(0.003)(100)(1.30)/(\text{g water-free soil})$$

$$= (10.0 - \text{meq Fe } SO_4)(0.003)(100)(1.30)/(\text{g water-free soil})$$

Note: 1.30 is an empirically obtained correction factor.

11. Calculate the normality of the ferrous sulfate solution as follows:

$$\text{Normality} = 10/(\text{vol})$$

where vol is the volume of ferrous ion solution required to titrate 10.0 ml 1 N $K_2Cr_2O_7$.

Note: Ferrous ammonium sulfate may be substituted for ferrous sulfate in this procedure.

References

"Walkley-Black Procedure" Section 29-3.5.2 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

Appendix C-8
Lab Procedure for Total Kjeldahl Nitrogen (TKN): Method AP-0064

1.0 PURPOSE

This procedure provides a method for the determination of total Kjeldahl nitrogen (TKN) in water and wastewater.

2.0 SCOPE

2.1 This method covers the determination of total Kjeldahl nitrogen in water and wastewater.

2.2 The colorimetric method is based on reactions that are specific for the ammonia ion. The digestion converts organic forms of nitrogen to the ammonium form. Nitrate is not converted to ammonium during digestion.

2.3 The applicable range is 0.1 to 20 mg N/L.

2.4 Samples containing particulates should be filtered or homogenized.

3.0 SUMMARY

3.1 The sample is heated in the presence of sulfuric acid, H_2SO_4, for two and one half hours. The residue is cooled, diluted with water and analyzed for ammonia. This digested sample may also be used for total phosphorus determination.

3.2 Total Kjeldahl nitrogen is the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of the digestion described.

3.3 Organic nitrogen is obtained by subtracting the free-ammonia concentration from the Kjeldahl nitrogen concentration.

3.4 Approximately 0.3 mL of the digested sample is injected onto the chemistry manifold where its pH is controlled by raising it to a known, basic pH by neutralization and with a concentrated buffer. This in-line neutralization converts the ammonium cation to ammonia, and also prevents undue influence of th

3.5 The ammonia thus produced is heated with salicylate and hypochlorite to produce blue color which is proportional to the ammonia concentration. The color is intensified by adding sodium nitroprusside. The presence of potassium tartrate in the buffer prevents precipitation of calcium and magnesium.

4.0 <u>REFERENCES</u>

4.1 U.S. Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, Revised March 1983, "Nitrogen, Kjeldahl, Total, Method 351.2 (Colorimetric, Semi-Automatic Block Digestor, AAII)."

4.2 U.S. Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, Revised March 1983, "Nitrogen, Ammonia, Method 350.1 (Colorimetric, Automated Phenate)."

4.3 ASTM , Water(I), Volume 11.01, Method D3590-89, "Test Methods for Kjeldahl Nitrogen in water", p. 447.

4.4 Code of Federal Regulations 40, Chapter 1, Part 136, Appendix B.

4.5 Lachat Instruments, *QuickChem Automated Ion Analyzer Methods Manual*, QuickChem Method 10-107-06-2-D, "Determination Of Total Kjeldahl Nitrogen By Flow Injection Analysis, Colorimetry (Block Digestor Method)."

4.6 Lachat Instruments, *QuickChem 8000 Automated Ion Analyzer Omnion FIA Software Installation and Tutorial Manual.*

5.0 <u>RESPONSIBILITIES</u>

5.1 It is the responsibility of the laboratory manager to ensure that this procedure is followed.

5.2 It is the responsibility of the team leader to review the results of the procedure.

5.3 It is the responsibility of the Analysts to follow this procedure, evaluate data, and to report any abnormal results or unusual occurrences to the team leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to ensure a representative sample and allow for quality control analysis (at least 100 mL).

6.1.2 Samples may be preserved by addition of a maximum of 2 mL of concentrated H_2SO_4 per liter (preferred - 1 mL of 1N H_2SO_4 per 100 mL) and stored at 4°C. Acid preserved samples have a holding time of 28 days.

6.2 Limitations and Actions

6.2.1 If the analyte concentration is above the analytical range of the calibration curve, the sample must be diluted with reagent 7 to bring the analyte concentration within range.

6.2.2 Interferences

6.2.2.1 Samples must not consume more than 10% of the sulfuric acid during digestion (one mL of sulfuric acid should remain after digestion). The buffer will accommodate a range of 4.5-5.0% (v/v) H_2SO_4 in the digested sample with no change in signal intensity.

6.2.2.2 High nitrate concentrations (10X or more than the TKN level) result in low TKN values. If interference is suspected, samples should be diluted and reanalyzed.

6.2.2.3 Digests must be free of turbidity. Some boiling stones have been shown to crumble upon vigorous vortexing.

6.3. Apparatus/Equipment

6.3.1 Balance – analytical, capable of accurately weighing to the nearest 0.0001 g.

6.3.2 Glassware – Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

6.3.3 Flow injection analysis equipment (Lachat model 8000) designed to deliver and react samples and reagents in the required order and ratios.

6.3.3.1 Autosampler

6.3.3.2 Multichannel proportioning pump

6.3.3.3 Reaction unit or manifold

6.3.3.4 Colorimetric detector

6.3.3.5 Data system

6.3.3.6 10 nm band pass, 80 uL, glass flow cell

6.3.3.7 660 nm interference filter

6.3.3.8 Helium degassing tube

6.3.4 Special Apparatus

6.3.4.1 Heating Unit

6.3.4.2 75 mL digestion tubes with cold fingers

6.3.4.3 Digestion tube rack

6.3.4.4 Cold finger rack assembly

6.3.4.5 Block Digestor

6.3.4.6 5 mL dispenser

6.3.4.7 10 mL dispenser

6.3.4.8 Vortex mixer

6.3.4.9 Countdown timer

6.4 Reagents and Standards

6.4.1 Preparation of Reagents -

Use deionized water (10 megohm) for all solutions.

Degassing with helium: To prevent bubble formation, degas all solutions with helium except the standards, Mercuric Sulfate Solution (Reagent 1) and Digestion Solution (Reagent 2). Bubble helium through a degassing tube (Lachat Part 50100) into the solution for at least one minute.

Refrigerate all solutions and standards.

6.4.1.1 **Reagent 1. Mercuric Sulfate Solution**

By Volume: To a **100 ml** volumetric flask add **40.0 mL water** and **10 mL concentrated sulfuric acid (H_2SO_4)**. Then add **8.0 g red mercuric oxide (HgO)**. Stir until dissolved, dilute to the mark and invert to mix. Warming the solution while stirring may be required to dissolve the mercuric oxide.

6.4.1.2 **Reagent 2 Digestion Solution**

By Volume: To a **1 L** volumetric flask, add **133.0 g potassium sulfate** (K_2SO_4) and **200 mL concentrated sulfuric acid** (H_2SO_4) to approximately **700 mL water**. Add **25.0 mL Reagent 1**. Dilute to the mark with water and invert to mix.

6.4.1.3 **Reagent 3. Buffer**

Note: To reduce the possibility of the potassium tartrate being contaminated, it is recommended that the tartrate buffer is boiled for 10 minutes. To verify that the tartrate buffer is pure enough, compare the reagent baseline to the DI water baseline. The baseline, with all reagents flowing should not be greater than 0.15V different from just the DI water pumping in all lines.

By Volume: In a **1L** container add **900 mL water, 50 g potassium tartrate** (or potassium sodium tartrate, $NaKC_4H_4O_6 \cdot 4H_2O$), **50 g sodium hydroxide** (NaOH), and **26.8 g sodium phosphate dibasic heptahydrate** ($Na_2HPO_4 \cdot 7H_2O$). Mix until dissolved. Boil for 10 minutes. Cool to room temperature and transfer to a **1L** volumetric flask. Dilute to the mark and invert to mix.

6.4.1.4 **Reagent 4. Sodium Hydroxide (0.8 M)**

By Volume: In a **1 L** volumetric flask dissolve **32 g sodium hydroxide** (NaOH) in about **800 mL of water**. Dilute to the mark and stir to mix.

By Weight: In a **1 L** container dissolve **32 g sodium hydroxide** (NaOH) in **985 g of water** and mix.

6.4.1.5 **Reagent 5. Salicylate Nitroprusside**

By Volume: In a **1 L** volumetric flask dissolve **150.0 g sodium salicylate** [salicylic acid sodium salt, $C_6H_4(OH)(COO)Na$], and **1.00 g sodium nitroprusside** [sodium nitroferricyanide dihydrate, $Na_2Fe(CN)_5NO \cdot 2H_2O$] in about **800 mL water**. Dilute to the mark and mix. Store in a dark bottle.

By Weight: To a tared **1 L** dark container, add **150.0 g sodium salicylate** [salicylic acid sodium salt, $C_6H_4(OH)(COO)Na$], and **1.00 g sodium nitroprusside** [sodium nitroferricyanide dihydrate, $Na_2Fe(CN)_5NO \cdot 2H_2O$] and **908 g water**. Mix and store in a dark bottle.

6.4.1.6 **Reagent 6. Hypochlorite Solution**

By Volume: In a **250 mL** volumetric flask, dilute **15.0 mL Regular Clorox Bleach** (5.25% sodium hypochlorite, The Clorox Company, Oakland CA) to the mark with water. Invert to mix.

By Weight: To a tared **250 mL** container, add **16 g of Regular Clorox Bleach** (5.25% sodium hypochlorite, The Clorox Company , Oakland CA) and **234 g water**. Shake to mix.

6.4.1.7 **Reagent 7. Diluent**

Note: Diluent is used for the **carrier** and for off line dilutions.

By Volume: In a **1 L** volumetric flask add about **700 mL water**, then add **48 mL concentrated sulfuric acid** (H_2SO_4), (CAUTION: The solution will get very hot!). Swirl to mix. When it can be comfortably handled, add **31.7 g potassium sulfate** (K_2SO_4). Dilute to the mark with water and mix.

By Weight: In a tared **1 L** container, add **940 g water** then **88.3 g concentrated sulfuric acid** (H_2SO_4), (CAUTION: The solution will get very hot!). Swirl to mix. When it can be comfortably handled, add **31.7 g potassium sulfate** (K_2SO_4) and mix.

6.4.2 Preparation of Standards

Note: Working standards are prepared per instructions below and then processed through the digestion procedure along with the samples.

6.4.2.1 **Standard 1. Stock Standard 1000 mg N/L**

Dry **ammonium chloride** (NH_4Cl) for two hours at 105°C. In a **1 L** volumetric flask dissolve **3.819 g ammonium chloride** (NH_4Cl) in about **800 mL water.** Dilute to mark with **water** and mix.. Refrigerate. This solution is stable for six months.

6.4.2.2 **Standard 2. Working Standard - 50 mg N/L**

In a **1 L** volumetric flask add about **600 mL water**. Pipette **50 mL** of the **1000 mg N/L** stock standard (standard 1), dilute to mark with **water** and mix.

6.4.2.3 **Standard 3. Working Quality Control Standard - 31.06 mg N/L**

In a **500 mL** volumetric flask add about **300 mL water**. Pipette **20 mL** of the E M Science **1000 mg N/L Ammonia Standard Solution** (776.5 mg N/L), dilute to mark with **water** and mix.

Note: 1000 mg/L standards by other reputable laboratory vendors may be substituted.

6.4.2.4 **Calibration Standards**

Standards are diluted to **500 mL** with **water**.

	Calibration Standards Concentration mg/L	Prepared From Concentration mg/L	Prepared From Aliquot mL
1	20.00	50	200
2	10.00	50	100
3	4.00	50	40
4	2.50	50	25
5	1.00	10	50
6	0.10	1	50
7	0.02	0.10	100
8	0.00	Water	0

6.4.2.5 **Laboratory Control Standard - 1.55 mg N/L**

In a **1 L** volumetric flask add about **700 mL water**. Pipette **50 mL** of the **Working Quality Control Standard** (standard 3). Dilute to mark with **water** and mix.

6.5 Quality Control Sample Requirements

Begin and end each run by measuring a laboratory control standard, a midpoint calibration standard run as a sample, and a reagent blank. When the run is long enough, every twentieth sample should be followed by the above three QC check samples. Recovery should be 90 to 110% of the expected value.

7.0 PROCEDURE

7.1 Procedure Instructions

7.1.1 Digestion Procedure

7.1.1.1 Both standards and samples are carried through this procedure.

7.1.1.2 Using a digestion tube rack to hold the digestion tubes, place **20.0 mL of sample** or standard in the digestion tubes. Use an acid resistant repipet device to add **5 mL of the digestion** solution (Reagent 2). Mix.

7.1.1.3 Add **2-4 Hengar granules** to each tube. Hengar granules are effective for smooth boiling.

7.1.1.4 Verify that boiling stones have been placed in each tube. Place tubes in the preheated block digestor for **one hour** at **160°C**. Water from the samples should have boiled off before increasing the temperature in step 7.1.1.5.

7.1.1.5 After the water has boiled off, place the **cold fingers** on the tubes. Continue to digest for **1.5 additional hours** with the controller set to **380°C**. This time includes the ramp time for the temperature to come up to 380°C. The typical ramp time is 50 - 60 minutes. 380°C must be maintained for 30 minutes.

7.1.1.6 Before removing samples, gather the necessary supplies to dilute the samples with water. Remove the samples from the digestion block and place on a rack stand. Allow tubes to cool for a minimum of **8 minutes**.

7.1.1.7 With the water dispenser calibrated for 10 mL, add **10 mL of water** to each tube.

7.1.1.8 Place the tubes on a block digestor that is heated to **105°C**. Let the tubes stay on the digestor three to five minutes, but no more than five minutes to avoid loss of volume. Remove the tubes to a tube rack stand.

7.1.1.9 Using a vortex mixer and a countdown timer, mix the samples two at a time for one minute. Do not let the unmixed samples remain unheated for more than three minutes. If there are a large number of samples, it will be necessary to return the tubes with unmixed samples back to the 105°C block digestor to keep the samples warm until mixed but for no more than three minutes at a time. Alternate placing the unmixed samples on and off of the heating block as needed until all samples are mixed. Caution must be given in not allowing the samples to get too cool, which will prevent the potassium sulfate and ammonium sulfate crystals from going into solution.

7.1.1.10 Hold the tubes up to a light source and swirl to see if there are any undissolved crystals in the solution (not to be confused with very fine boiling stone residue). If crystals are present, reheat and remix.

7.1.1.11 After all of the samples have been mixed, use the water dispenser to add an addition **10 mL of water** to each tube. The total final volume should be 21 mL. Mix well using the vortex mixer.

7.1.1.12 Allow the samples to cool to room temperature and analyze.

7.1.2 Analysis Procedure

7.1.2.1 The instrument is calibrated each day of use and may be calibrated with each sample tray.

7.1.2.2 Prepare reagents and standards as described in section 6.4

7.1.2.3 Set up manifold as shown in section 9.2

7.1.2.4 Enter data system parameters as in section 9.1

7.1.2.5 Pump deionized water through all reagent lines and check for leaks and smooth flow. Allow 15 minutes for heating unit to warm up to 60°C. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved. Add the buffer line first, pump for about 5 minutes or at least until the air bubbles introduced during the transfer passes through the flow cell. Then place all other transmission lines in the proper reagents.

7.1.2.6 Load standard and sample trays.

7.1.2.7 Place samples and standards in the autosampler. Enter the information required by the data system, such as standard concentration, and sample identification.

7.1.2.8 Calibrate the instrument by injecting the standards. The data system will then associate the concentration with the instrument responses for each standard.

7.1.2.9 After the standards are injected and the system has automatically prepared a calibration curve, the system will inject the samples from the sample tray.

7.1.2.10 If the analyte concentration is above the analytical range of the calibration curve, the sample must be diluted with reagent 7 to bring the analyte concentration within range.

7.1.2.11 At the end of the run, remove all transmission lines from reagents and place them in water. Pump for about five minutes.

7.1.2.12 To prevent baseline drifts, peaks that are too wide, or other problems with precision, clean the manifold by placing the manifold reagent lines in 1 M hydrochloric acid (1 volume of concentrated HCl added to 11 volumes of water). Pump for about five minutes.

7.1.2.13 Remove all reagent lines from the hydrochloric acid and place them in water. Pump until the HCl is thoroughly washed out (about 5 minutes).

7.1.2.14 Remove the transmission lines from the water and pump all lines dry.

7.2 Calculations and Recording Data

7.2.1 Calibration is done by injecting standards. The data system will then automatically prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation provided by the software.

7.2.2 Create a custom report. (Lachat Instruments, *QuickChem 8000 Automated Ion Analyzer Orion FIA Software Installation and Tutorial Manual,* page 43, "Task 11 - Creating a Custom Report")

7.2.3 Report on those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard must be diluted with reagent 7 and reanalyzed.

7.2.4 Report results in mg N/L.

8.0 SAFETY

8.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Use routine laboratory protective clothing (lab coat, gloves, and eye protection) when handling these reagents. Thoroughly wash any skin that comes into contact with any of these chemicals. Avoid creating of inhaling dust or fumes from solid chemicals.

9.0 NOTES

9.1 Data System Parameters

Method Filename:	TN_D.MET
Method Description:	TKN (d) = 20.0 to 0.1 mg N/L
Analyte Data:	
Analyte Name:	Total N
Concentration Units:	mg N/L
Chemistry:	Direct
Inject to Peak Start (s):	42.0
Peak Base Width (s):	39.000
% Width Tolerance:	100.000
Threshold:	8000.000
Autodilution Trigger:	Off
QuickChem Method:	10-107-06-2-D

Calibration Data:

Levels: (mg N/L)	1: 20.000	2: 10.000	3. 4.000
	4: 1.000	5: 0.100	6. 0.000

Calibration Rep Handling: Average

Calibration Fit Type: 1st Order Poly

Force Through Zero: No

Weighing Method: None

Concentration Scaling: None

Sampler Timing:

Method Cycle Period (s): 55.0

Min. Probe in Wash Prd. (s): 9.0

Probe in Sample Period (s): 25.0

Valve Timing:

Method Cycle Period (s): 55.0

Sample Reaches 1st Valve (s): 19.0

Valve: On

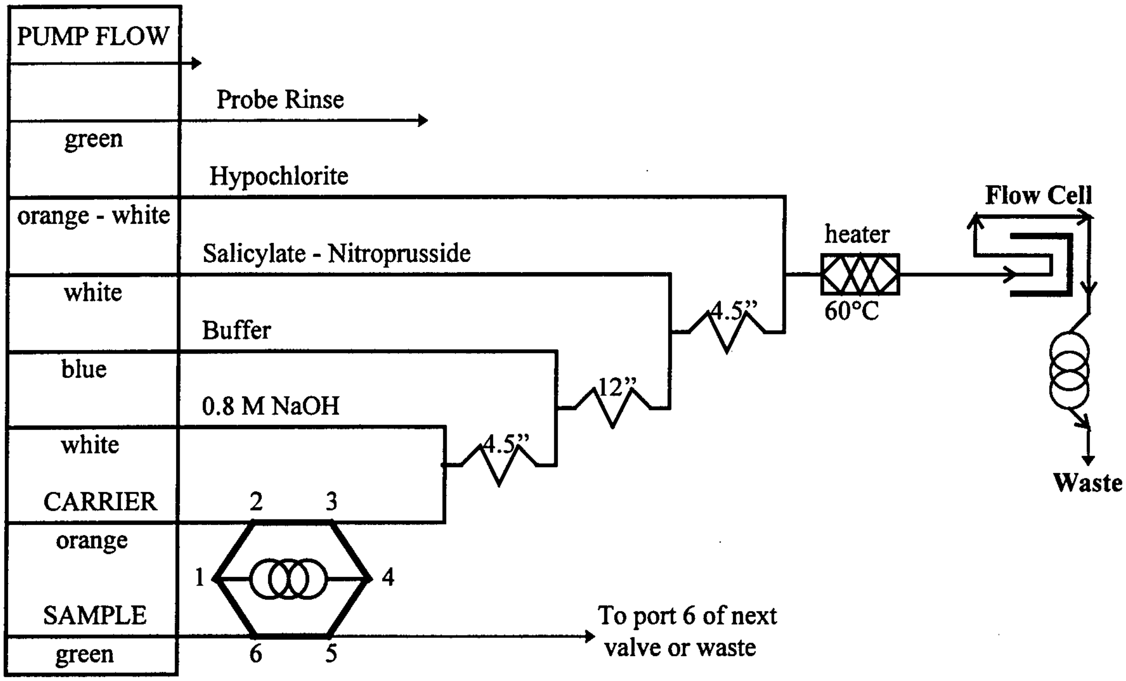
Load Time (s): 0.0

Load period (s): 20.0

Inject Period (s): 35.0

Sample Loop: 50 cm

9.2 Total Kjeldahl Nitrogen Manifold Diagram



Sample Loop = 50 cm

Interference Filter = 660 nm

Carrier is Diluent (reagent 7)

All manifold tubing is **0.8 mm (0.32 in) i.d.** Lachat Part No. 50028. This is **5.2 uL/cm**

4.5 is **70 cm** of tubing on a **4.5 cm** coil support.

12 is **255 cm** of tubing on a **12 cm** coil support.

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The  60°C includes 650 cm of tubing wrapped around the heater block at 60°C.

10.0 ATTACHMENTS AND APPENDICES

None

End of Procedure

Appendix C-9
Lab Procedure for Extractable P: Method ASA 24-5.2

Phosphorus Soluble in Dilute Hydrochloric Acid and Sulfuric Acid
or
Mehlich I (North Carolina Double Acid) P Determination in Soil

ASA 24-5.2

Reagents:

1. Extraction Solution: Add 12 ml of concentrated H_2SO_4 and 73 ml of concentrated HCl to approximately 15 liters of deionized water. Make to 18 liters. This solution is approximately 0.05 N HCl and 0.025 N H_2SO_4. Smaller quantities may be made in the same ratio.

Procedure:

1. Weigh 12.5 g of soil to a 125-ml Erlenmeyer flask.

2. Add 50.0 ml of extracting solution.

3. Shake on oscillating shaker at 180 oscillations per minute for exactly 5 minutes.

4. Filter through Whatman 42 filter paper into a 50-ml Erlenmeyer flask.

5. Submit the filtrates for analysis by inductively coupled plasma (ICP), atomic absorption, or spectrometric methods.

References:

"Phosphorus Soluble in Dilute Hydrochloric Acid and Sulfuric Acid," Section 24-5.2 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

Appendix C-10
Lab Procedure for Exchangeable K, Ca, and Mg: Method ASA 9-3.1

Determination of Exchangeable Cations in Soils Without Determining Total CEC

Ammonium Acetate Extraction

ASA 9-3.1

Reagent:

1. 1N Ammonium Acetate - Dissolve 231.34 g of reagent grade ammonium acetate in 2 liters of deionized water. Make to a 3 liter volume. Place beaker on a stirrer, insert electrodes in the solution and adjust pH to 7.0 with concentrated ammonium hydroxide or glacial acetic acid. For an 18 liter volume dissolve 1388.04 g of ammonium acetate. (Other volumes may be made in the same ratio.)

Procedure:

1. Weigh 5 g of soil (-2 mm, which is -9 mesh) into 125 ml Erlenmeyer flask.

2. Add 50 ml of 1N ammonium acetate, shake for 30 minutes on oscillating shaker on low setting (180/min).

3. Let stand at least 6 hours, preferably overnight, occasionally swirling the flasks.

4. Filter through Whatman 40 filter paper into 50 ml Erlenmeyer flask.

5. Submit the filtrates for analysis by inductively coupled plasma (ICP) or atomic absorption.

6. Convert soil ppm to centimols (cmol) per kg (report to a hundredth of a cmol).

Examples:

Cation	Divide soil ppm by
Ca	400
Mg	242
K	391
Mn	549

References:

"Replacement of Exchangeable Cations, Ammonium Acetate Method" Section 9-3.1 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

Appendix C-11
Lab Procedure for Exchangeable Al: Method ASA 9-4.2

Exchangeable Aluminum by One Normal Potassium Chloride Extraction
ASA 9-4.2

Reagents: 1N KCl - Dissolve 74.0 grams potassium chloride in about 800 ml of deionized water. Dilute to 1 liter.

Procedure:

1. Weigh 5 grams soil into a 250 ml centrifuge tube.

2. Add 50 ml 1N KCl to each sample.

3. Shake for 30 minutes at 180/min setting.

4. Centrifuge for 5 minutes at 1500 rpm.

5. Filter through Whatman 42 filter paper into a 50ml Erlenmeyer flask.

6. Submit the sample for aluminum analysis by ICP.

References:

Can. J. Soil Sci. 70:263-275

"Exchangeable Acidity, Potassium Chloride Method," Section 9-4.2 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

Appendix C-12
Lab Procedure for DTPA - Extractable Fe and Mn: Method ASA 17-4.3

DTPA Extraction of Soils
ASA 17-4.3

Reagent:

DTPA Extraction Solution (0.005M DTPA, 0.01M Calcium Chloride, 0.1M TEA)

1. Add 600 ml deionized water to a 1 liter volumetric flask.
2. Add 14.9 g TEA (Triethanolamine) and dissolve (add 16.5 ml if liquid form used).
3. Add 1.970 g of diethylene triamine pentaacetic acid and dissolve.
4. Add 1.470 g of calcium chloride and dissolve.
5. Bring volume to about 970 ml with deionized water.
6. Transfer to a beaker and adjust to pH of 7.3 with 6N HCl (about 13 ml required).
7. Return to volumetric flask and bring to volume.

Procedure:

1. Place 10 g dry soil in 125 ml Erlenmeyer flask.
2. Add 20 ml of DTPA extracting solution.
3. Shake for 2 hours on an oscillating shaker on low setting (180/min).
4. Filter extract through previously folded Whatman 42 filter paper into a 50 ml Erlenmeyer flask.
5. Submit the filtrates for analysis by inductively coupled plasma (ICP), atomic absorption, or spectrometric methods.

References:

"Availability Indices," Section 17-4.3 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

Appendix C-13
Lab Procedure for Total Metals: Method 3005A

Method 3005A -Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy

1.0 Procedure

Prepare liquid samples for further analysis by AA or ICP in accordance with Method 3005A from SW-846 as attached.

2.0 Recordkeeping

Retain all machine printouts, worksheets, percent recovery calculations of quality control samples, and notes.

3.0 Quality Control Samples

For each batch of samples, perform the quality control analyses specified in the method:

- method blank
- reagent blank
- calibration check sample.

For each batch introduce one quality control sample made from a separate stock than that used to calibrate the machine.

Where possible, for each batch analyze one matrix spike sample.

For each batch analyze a matrix spike duplicate or sample duplicate.

METHOD 3005A

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Method 3005 is an acid digestion procedure used to prepare surface and ground water samples for analysis by flame atomic absorption spectroscopy (FLAA) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3005 may be analyzed by AAS or ICP for the following metals:

Aluminum	Magnesium
Antimony**	Manganese
Arsenic*	Molybdenum
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium*
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* ICP only
**May be analyzed by ICP, FLAA, or GFAA

1.2 When analyzing for total dissolved metals filter the sample, at the time of collection, prior to acidification with nitric acid.

2.0 SUMMARY OF METHOD

2.1 Total recoverable metals - The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals - The sample is filtered through a 0.45-μm filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards.

3.0 INTERFERENCES

3.1 The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

Precipitation will cause a lowering of the silver concentration and therefore an inaccurate analysis.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers of assorted sizes or equivalent.

4.2 Watch glasses or equivalent.

4.3 Qualitative filter paper and filter funnels.

4.4 Graduated cylinder or equivalent.

4.5 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Both plastic and glass containers are suitable.

6.3 Sampling

6.3.1 Total recoverable metals - All samples must be acidified at the time of collection with HNO_3 (5 mL/L).

6.3.2 Dissolved metals - All samples must be filtered through a 0.45-μm filter and then acidified at the time of collection with HNO_3 (5 mL/L).

7.0 PROCEDURE

7.1 Transfer a 100-mL aliquot of well-mixed sample to a beaker.

7.2 For metals that are to be analyzed, add 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl. The sample is covered with a ribbed watch glass or other suitable covers and heated on a steam bath, hot plate or other heating source at 90 to 95°C until the volume has been reduced to 15-20 mL.

<u>CAUTION</u>: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

7.3 Remove the beaker and allow to cool. Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.

7.4 Adjust the final volume to 100 mL with reagent water.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. Replicate samples will be used to determine precision. The sample load will dictate the frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch. Refer to Chapter One for the proper protocol when analyzing spikes.

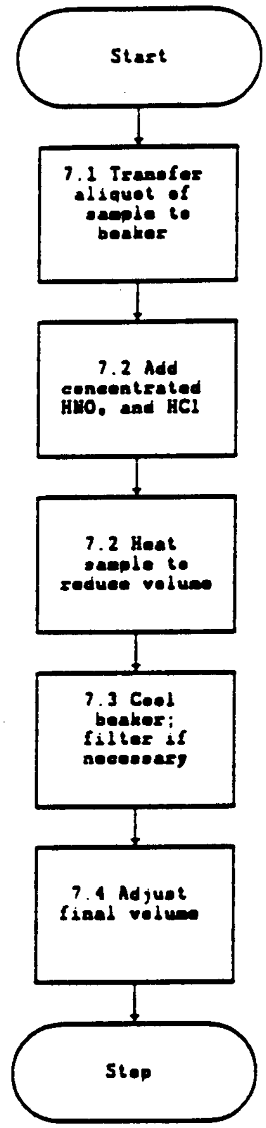
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Transfer aliquot of sample to beaker
7.2 Add concentrated HNO_3 and HCl
7.2 Heat sample to reduce volume
7.3 Cool beaker; filter if necessary
7.4 Adjust final volume
Stop

METHOD 3005A

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Method 3005 is an acid digestion procedure used to prepare surface and ground water samples for analysis by flame atomic absorption spectroscopy (FLAA) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3005 may be analyzed by AAS or ICP for the following metals:

Aluminum	Magnesium
Antimony**	Manganese
Arsenic*	Molybdenum
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium*
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* ICP only
**May be analyzed by ICP, FLAA, or GFAA

1.2 When analyzing for total dissolved metals filter the sample, at the time of collection, prior to acidification with nitric acid.

2.0 SUMMARY OF METHOD

2.1 Total recoverable metals - The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals - The sample is filtered through a 0.45-μm filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards.

3.0 INTERFERENCES

3.1 The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

Precipitation will cause a lowering of the silver concentration and therefore an inaccurate analysis.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers of assorted sizes or equivalent.

4.2 Watch glasses or equivalent.

4.3 Qualitative filter paper and filter funnels.

4.4 Graduated cylinder or equivalent.

4.5 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Both plastic and glass containers are suitable.

6.3 Sampling

6.3.1 Total recoverable metals - All samples must be acidified at the time of collection with HNO_3 (5 mL/L).

6.3.2 Dissolved metals - All samples must be filtered through a 0.45-μm filter and then acidified at the time of collection with HNO_3 (5 mL/L).

7.0 PROCEDURE

7.1 Transfer a 100-mL aliquot of well-mixed sample to a beaker.

7.2 For metals that are to be analyzed, add 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl. The sample is covered with a ribbed watch glass or other suitable covers and heated on a steam bath, hot plate or other heating source at 90 to 95°C until the volume has been reduced to 15-20 mL.

<u>CAUTION</u>: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

7.3 Remove the beaker and allow to cool. Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.

7.4 Adjust the final volume to 100 mL with reagent water.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. Replicate samples will be used to determine precision. The sample load will dictate the frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch. Refer to Chapter One for the proper protocol when analyzing spikes.

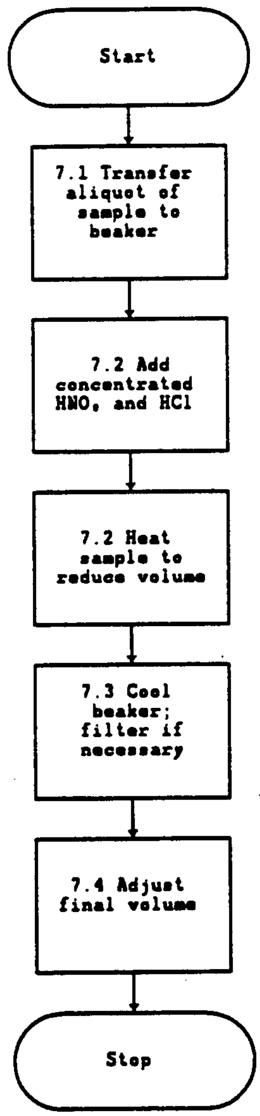
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Transfer aliquot of sample to beaker
7.2 Add concentrated HNO_3 and HCl
7.2 Heat sample to reduce volume
7.3 Cool beaker; filter if necessary
7.4 Adjust final volume
Stop

Appendix C-14
Lab Procedure for Total Metals: Method 3050B

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method has been written to provide two separate digestion procedures, one for the preparation of sediments, sludges, and soil samples for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES) and one for the preparation of sediments, sludges, and soil samples for analysis of samples by Graphite Furnace AA (GFAA) or inductively coupled plasma mass spectrometry (ICP-MS). The extracts from these two procedures are not interchangeable and should only be used with the analytical determinations outlined in this section. Samples prepared by this method may be analyzed by ICP-AES or GFAA for all the listed metals as long as the detecion limits are adequate for the required end-use of the data. Alternative determinative techniques may be used if they are scientifically valid and the QC criteria of the method, including those dealing with interferences, can be achieved. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest (See Section 8.0). The recommended determinative techniques for each element are listed below:

FLAA/ICP-AES		GFAA/ICP-MS
Aluminum	Magnesium	Arsenic
Antimony	Manganese	Beryllium
Barium	Molybdenum	Cadmium
Beryllium	Nickel	Chromium
Cadmium	Potassium	Cobalt
Calcium	Silver	Iron
Chromium	Sodium	Lead
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		
Vanadium		

1.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment. If absolute total digestion is required use Method 3052.

2.0 SUMMARY OF METHOD

2.1 For the digestion of samples, a representative 1-2 gram (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2).

2.2 For GFAA or ICP-MS analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 mL.

2.3 For ICP-AES or FLAA analyses, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals (see Section 7.3.1: NOTE), this digestate is filtered and the filter paper and residues are rinsed, first

with hot HCl and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional HCl and then filtered again. The digestate is then diluted to a final volume of 100 mL.

2.4 If required, a separate sample aliquot shall be dried for a total percent solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements given in Sec. 8.0 to aid in determining whether Method 3050B is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

4.1 Digestion Vessels - 250-mL.

4.2 Vapor recovery device (e.g., ribbed watch glasses, appropriate refluxing device, appropriate solvent handling system).

4.3 Drying ovens - able to maintain 30°C $\pm$ 4°C.

4.4 Temperature measurement device capable of measuring to at least 125°C with suitable precision and accuracy (e.g., thermometer, IR sensor, thermocouple, thermister, etc.)

4.5 Filter paper - Whatman No. 41 or equivalent.

4.6 Centrifuge and centrifuge tubes.

4.7 Analytical balance - capable of accurate weighings to 0.01 g.

4.8 Heating source - Adjustable and able to maintain a temperature of 90-95°C. (e.g., hot plate, block digestor, microwave, etc.)

4.9 Funnel or equivalent.

4.10 Graduated cylinder or equivalent volume measuring device.

4.11 Volumetric Flasks - 100-mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.5 Hydrogen peroxide (30%), H_2O_2. Oxidant should be analyzed to determine level of impurities. If method blank is < MDL, the peroxide can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be demonstrated to be free of contamination at or below the reporting limit. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

6.3 Nonaqueous samples should be refrigerated upon receipt and analyzed as soon as possible.

6.4 It can be difficult to obtain a representative sample with wet or damp materials. Wet samples may be dried, crushed, and ground to reduce subsample variability as long as drying does not affect the extraction of the analytes of interest in the sample.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity and sieve, if appropriate and necessary, using a USS #10 sieve. All equipment used for homogenization should be cleaned according to the guidance in Sec. 6.0 to minimize the potential of cross-contamination. For each digestion procedure, weigh to the nearest 0.01 g and transfer a 1-2 g sample (wet weight) or 1 g sample (dry weight) to a digestion vessel. For samples with high liquid content, a larger sample size may be used as long as digestion is completed.

> NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. The use of an acid vapor scrubber system for waste minimization is encouraged.

7.2 For the digestion of samples for analysis by GFAA or ICP-MS, add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass or vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL of conc. HNO_3) over and over until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a ribbed watch glass or vapor recovery system, either allow the solution to evaporate to approximately 5 mL without boiling or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by GFAA or ICP-MS by adding 10 mL of 1:1 HNO_3, mixing the slurry and then covering with a vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C without boiling. Allow the sample to cool for 5 minutes, add 5 mL of concentrated HNO_3, heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL concentrated HNO_3) until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a vapor recovery system, heat the sample to 95°C ± 5°C and reflux for 10 minutes at 95°C ± 5°C without boiling.

7.2.1 After the step in Section 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H_2O_2. Cover the vessel with a watch glass or vapor recovery device and return the covered vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the vessel.

NOTE: Alternatively, for direct energy coupled devices: After the Sec. 7.2 "NOTE" step has been completed and the sample has cooled for 5 minutes, add slowly 10 mL of 30% H_2O_2. Care must be taken to ensure that losses do not occur due to excessive vigorous effervesence. Go to Section 7.2.3.

7.2.2 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

7.2.3 Cover the sample with a ribbed watch glass or vapor recovery device and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupled devices: Heat the acid-peroxide digestate to 95°C ± 5°C in 6 minutes and remain at 95°C ± 5°C without boiling for 10 minutes.

7.2.4 After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle. The sample is now ready for analysis by GFAA or ICP-MS.

7.2.4.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.2.4.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.2.4.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier.

7.3 For the analysis of samples for FLAA or ICP-AES, add 10 mL conc. HCl to the sample digest from 7.2.3 and cover with a watch glass or vapor recovery device. Place the sample on/in the heating source and reflux at 95°C ± 5°C for 15 minutes.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by FLAA and ICP-AES by adding 5 mL HCl and 10 mL H_2O to the sample digest from 7.2.3 and heat the sample to 95°C ± 5°C, Reflux at 95°C ± 5°C without boiling for 5 minutes.

7.4 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Make to volume and analyze by FLAA or ICP-AES.

NOTE: Section 7.5 may be used to improve the solubilities and recoveries of antimony, barium, lead, and silver when necessary. These steps are optional and are not required on a routine basis.

7.5 Add 2.5 mL conc. HNO_3 and 10 mL conc. HCl to a 1-2 g sample (wet weight) or 1 g sample (dry weight) and cover with a watchglass or vapor recovery device. Place the sample on/in the heating source and reflux for 15 minutes.

7.5.1 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5 mL of hot (~95°C) HCl, then with 20 mL of hot (~95°C) reagent water. Collect washings in the same 100-mL volumetric flask.

7.5.2 Remove the filter and residue from the funnel, and place them back in the vessel. Add 5 mL of conc. HCl, place the vessel back on the heating source, and heat at 95°C ± 5°C until the filter paper dissolves. Remove the vessel from the heating source and wash the cover and sides with reagent water. Filter the residue and collect the filtrate in the same 100-mL volumetric flask. Allow filtrate to cool, then dilute to volume.

NOTE: High concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates upon cooling of primary and/or secondary filtrates. If precipitation occurs in the flask upon cooling, do not dilute to volume.

7.5.3 If a precipitate forms on the bottom of a flask, add up to 10 mL of concentrated HCl to dissolve the precipitate. After precipitate is dissolved, dilute to volume with reagent water. Analyze by FLAA or ICP-AES.

7.6 Calculations

7.6.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.6.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, a method blank should be carried throughout the entire sample preparation and analytical process according to the frequency described in Chapter One. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing method blanks.

8.3 Spiked duplicate samples should be processed on a routine basis and whenever a new sample matrix is being analyzed. Spiked duplicate samples will be used to determine precision and bias. The criteria of the determinative method will dictate frequency, but 5% (one per batch) is recommended or whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spiked replicates.

8.4 Limitations for the FLAA and ICP-AES optional digestion procedure. Analysts should be aware that the upper linear range for silver, barium, lead, and antimony may be exceeded with some samples. If there is a reasonable possibility that this range may be exceeded, or if a sample's analytical result exceeds this upper limit, a smaller sample size should be taken through the entire procedure and re-analyzed to determine if the linear range has been exceeded. The approximate linear upper ranges for a 2 gram sample size:

Ag	2,000 mg/kg
As	1,000,000 mg/kg
Ba	2,500 mg/kg
Be	1,000,000 mg/kg
Cd	1,000,000 mg/kg
Co	1,000,000 mg/kg
Cr	1,000,000 mg/kg
Cu	1,000,000 mg/kg
Mo	1,000,000 mg/kg
Ni	1,000,000 mg/kg
Pb	200,000 mg/kg
Sb	200,000 mg/kg
Se	1,000,000 mg/kg
Tl	1,000,000 mg/kg
V	1,000,000 mg/kg
Zn	1,000,000 mg/kg

NOTE: These ranges will vary with sample matrix, molecular form, and size.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, the recoveries of the three matrices presented in Table 2 were obtained using the digestion procedure outlined for samples prior to analysis by FLAA and ICP-AES. The spiked samples were analyzed in duplicate. Tables 3-5 represents results of analysis of NIST Standard Reference Materials that were obtained using both atmospheric pressure microwave digestion techniques and hot-plate digestion procedures.

10.0 REFERENCES

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TABLE 1

STANDARD RECOVERY (%) COMPARISON FOR
METHODS 3050A AND 3050B[a]

Analyte	METHOD 3050A[a]	METHOD 3050B w/option[a]
Ag	9.5	98
As	86	102
Ba	97	103
Be	96	102
Cd	101	99
Co	99	105
Cr	98	94
Cu	87	94
Mo	97	96
Ni	98	92
Pb	97	95
Sb	87	88
Se	94	91
Tl	96	96
V	93	103
Zn	99	95

[a] All values are percent recovery. Samples: 4 mL of 100 mg/mL multistandard; n = 3.

TABLE 2

PERCENT RECOVERY COMPARISON FOR METHODS 3050A AND 3050B

Analyte	Sample 4435		Sample 4766		Sample HJ		Average	
	Percent Recovery[a,c]							
	3050A	3050B	3050A	3050B	3050A	3050B	3050A	3050B
Ag	9.8	103	15	89	56	93	27	95
As	70	102	80	95	83	102	77	100
Ba	85	94	78	95	b	b	81	94
Be	94	102	108	98	99	94	99	97
Cd	92	88	91	95	95	97	93	94
Co	90	94	87	95	89	93	89	94
Cr	90	95	89	94	72	101	83	97
Cu	81	88	85	87	70	106	77	94
Mo	79	92	83	98	87	103	83	98
Ni	88	93	93	100	87	101	92	98
Pb	82	92	80	91	77	91	81	91
Sb	28	84	23	77	46	76	32	79
Se	84	89	81	96	99	96	85	94
Tl	88	87	69	95	66	67	74	83
V	84	97	86	96	90	88	87	93
Zn	96	106	78	75	b	b	87	99

a - Samples: 4 mL of 100 mg/mL multi-standard in 2 g of sample. Each value is percent recovery and is the average of duplicate spikes.

b - Unable to accurately quantitate due to high background values.

c - Method 3050B using optional section.

Table 3
Results of Analysis of Nist Standard Reference Material 2704
"River Sediment" Using Method 3050B (µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	101 ± 7	89 ± 1	98 ± 1.4	100 ± 2	98.6 ± 5.0
Pb	160 ± 2	145 ± 6	145 ± 7	146 ± 1	161 ± 17
Zn	427 ± 2	411 ± 3	405 ± 14	427 ± 5	438 ± 12
Cd	NA	3.5 ± 0.66	3.7 ± 0.9	NA	3.45 ± 0.22
Cr	82 ± 3	79 ± 2	85 ± 4	89 ± 1	135 ± 5
Ni	42 ± 1	36 ± 1	38 ± 4	44 ± 2	44.1 ± 3.0

NA - Not Available

Table 4
Results of Analysis of NIST Standard Reference Material 2710
"Montana Soil (Highly Elevated Trace Element Concentrations)" Using Method 3050B
(µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	2640 ± 60	2790 ± 41	2480 ± 33	2910 ± 59	2700	2950 ± 130
Pb	5640 ± 117	5430 ± 72	5170 ± 34	5720 ± 280	5100	5532 ± 80
Zn	6410 ± 74	5810 ± 34	6130 ± 27	6230 ± 115	5900	6952 ± 91
Cd	NA	20.3 ± 1.4	20.2 ± 0.4	NA	20	21.8 ± 0.2
Cr	20 ± 1.6	19 ± 2	18 ± 2.4	23 ± 0.5	19	39*
Ni	7.8 ± 0.29	10 ± 1	9.1 ± 1.1	7 ± 0.44	10.1	14.3 ± 1.0

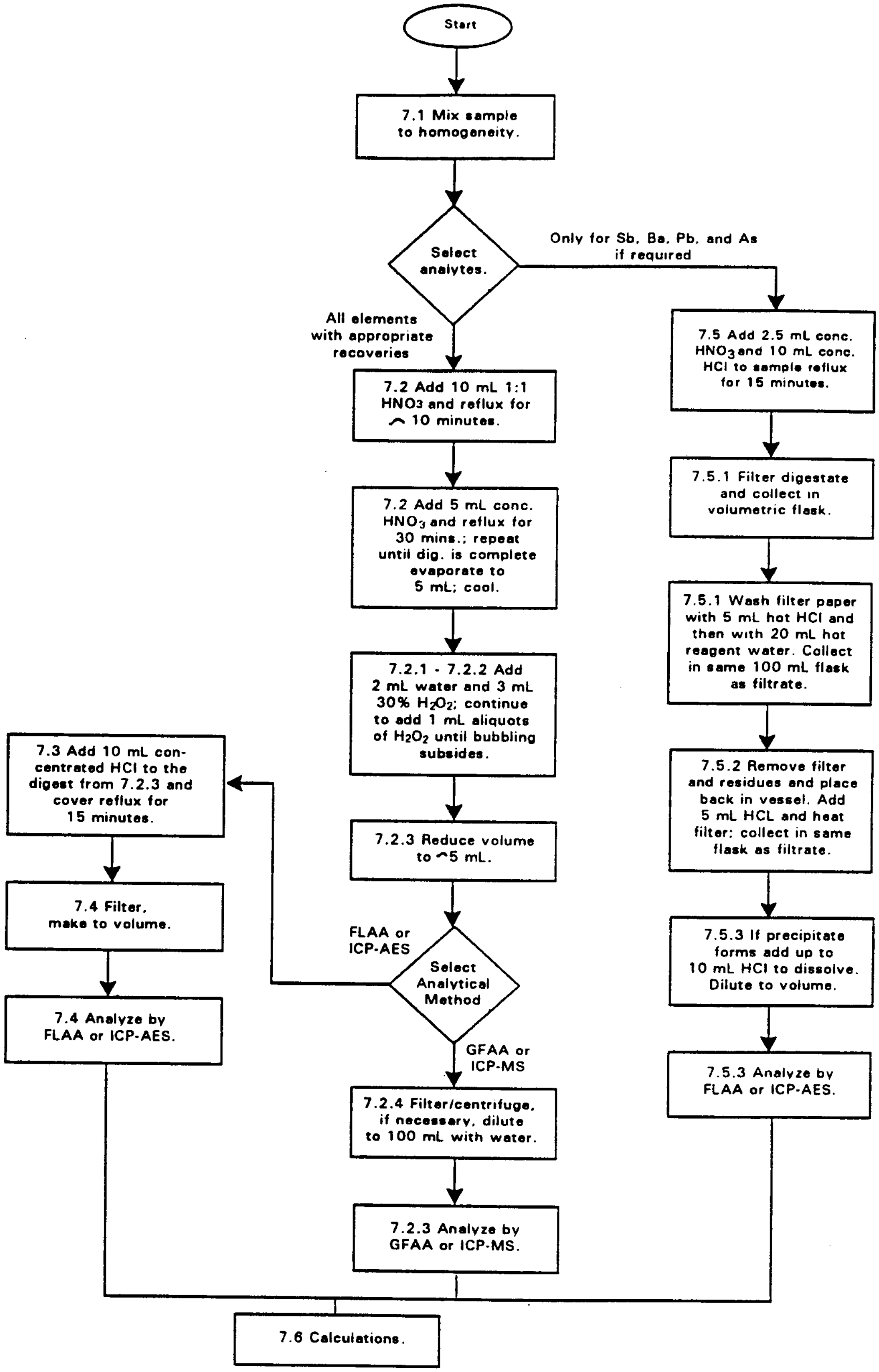
NA - Not Available

* Non-certified values, for information only.

Table 5
Results of Analysis of NIST Standard Reference Material 2711
"Montana Soil (Moderately Elevated Trace Element Concentrations)" Using Method 3050B
(µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	107 ± 4.6	98 ± 5	98 ± 3.8	111 ± 6.4	100	114 ± 2
Pb	1240 ± 68	1130 ± 20	1120 ± 29	1240 ± 38	1100	1162 ± 31
Zn	330 ± 17	312 ± 2	307 ± 12	340 ± 13	310	350.4 ± 4.8
Cd	NA	39.6 ± 3.9	40.9 ± 1.9	NA	40	41.7 ± 0.25
Cr	22 ± 0.35	21 ± 1	15 ± 1.1	23 ± 0.9	20	47*
Ni	15 ± 0.2	17 ± 2	15 ± 1.6	16 ± 0.4	16	20.6 ± 1.1

NA - Not Available
* Non-certified values, for information only.


Start
7.1 Mix sample to homogeneity.
Select analytes.
Only for Sb, Ba, Pb, and As if required
All elements with appropriate recoveries
7.2 Add 10 mL 1:1 HNO3 and reflux for ~ 10 minutes.
7.2 Add 5 mL conc. HNO3 and reflux for 30 mins.; repeat until dig. is complete evaporate to 5 mL; cool.
7.2.1 - 7.2.2 Add 2 mL water and 3 mL 30% H2O2; continue to add 1 mL aliquots of H2O2 until bubbling subsides.
7.2.3 Reduce volume to ~5 mL.
Select Analytical Method
FLAA or ICP-AES
GFAA or ICP-MS
7.2.4 Filter/centrifuge, if necessary, dilute to 100 mL with water.
7.2.3 Analyze by GFAA or ICP-MS.
7.3 Add 10 mL concentrated HCl to the digest from 7.2.3 and cover reflux for 15 minutes.
7.4 Filter, make to volume.
7.4 Analyze by FLAA or ICP-AES.
7.5 Add 2.5 mL conc. HNO3 and 10 mL conc. HCl to sample reflux for 15 minutes.
7.5.1 Filter digestate and collect in volumetric flask.
7.5.1 Wash filter paper with 5 mL hot HCl and then with 20 mL hot reagent water. Collect in same 100 mL flask as filtrate.
7.5.2 Remove filter and residues and place back in vessel. Add 5 mL HCL and heat filter; collect in same flask as filtrate.
7.5.3 If precipitate forms add up to 10 mL HCl to dissolve. Dilute to volume.
7.5.3 Analyze by FLAA or ICP-AES.
7.6 Calculations.

Appendix C-15
Lab Procedure for Total Metals: Method 6010B

METHOD 6010B

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. Groundwater samples that have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Refer to Chapter Three for the appropriate digestion procedures.

1.2 Table 1 lists the elements for which this method is applicable. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Table 1 lists the recommended analytical wavelengths and estimated instrumental detection limits for the elements in clean aqueous matrices. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices. Elements and matrices other than those listed in Table 1 may be analyzed by this method if performance at the concentration levels of interest (see Section 8.0) is demonstrated.

1.3 Users of the method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g. Chapter Three). When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in background

intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Section 8.5. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

3.0 INTERFERENCES

3.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

3.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

3.1.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration, a more appropriate test would be to use a concentration near the upper analytical range limit.

3.1.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction **require** the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement

correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Table 2. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

3.1.4 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary.

3.1.5 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.

3.1.6 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences (Table 2) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

3.1.7 Users of sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

3.1.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

3.1.9 When interelement corrections are applied, their accuracy should be verified, daily, by analyzing spectral interference check solutions. If the correction factors or multivariate correction matrices tested on a daily basis are found to be within the 20% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. Standard solution should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

3.1.10 When interelement corrections are <u>not</u> used, verification of absence of interferences is required.

3.1.10.1 One method is to use a computer software routine for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, (i.e., greater than) the analyte instrument detection limit, or false negative analyte concentration, (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

3.1.10.2 Another method is to analyze an Interference Check Solution(s) which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is ≥ 20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate

and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance: this may be accomplished with the use of mass flow controllers. The test described in Section 8.5.1 will help determine if a physical interference is present.

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

3.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.

3.5 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

3.6 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

4.1.1 Computer-controlled emission spectrometer with background correction.

4.1.2 Radio-frequency generator compliant with FCC regulations.

4.1.3 Optional mass flow controller for argon nebulizer gas supply.

4.1.4 Optional peristaltic pump.

4.1.5 Optional Autosampler.

4.1.6 Argon gas supply - high purity.

4.2 Volumetric flasks of suitable precision and accuracy.

4.3 Volumetric pipets of suitable precision and accuracy.

5.0 REAGENTS

5.1 Reagent or trace metals grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration of the contamination is less than the MDL then the reagent is acceptable.

5.1.1 Hydrochloric acid (conc), HCl.

5.1.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriately sized beaker.

5.1.3 Nitric acid (conc), HNO_3.

5.1.4 Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 liter in an appropriately sized beaker.

5.2 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra- high purity grade chemicals or metals (99.99% pure or greater). All salts must be dried for 1 hour at 105°C, unless otherwise specified.

Note: This section does not apply when analyzing samples that have been prepared by Method 3040.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the element fraction and the weight of the metal salt added.

For metals:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

For metal salts:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

5.3.1 Aluminum solution, stock, 1 mL = 1000 µg Al: Dissolve 1.000 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4.0 mL of (1:1) HCl and 1.0 mL of concentrated HNO_3 in a beaker. Warm beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1-liter flask, add an additional 10.0 mL of (1:1) HCl and dilute to volume with reagent water.

NOTE: Weight of analyte is expressed to four significant figures for consistency with the weights below because rounding to two decimal places can contribute up to 4 % error for some of the compounds.

5.3.2 Antimony solution, stock, 1 mL = 1000 µg Sb: Dissolve 2.6673 g $K(SbO)C_4H_4O_6$ (element fraction Sb = 0.3749), weighed accurately to at least four significant figures, in water, add 10 mL (1:1) HCl, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.3 Arsenic solution, stock, 1 mL = 1000 µg As: Dissolve 1.3203 g of As_2O_3 (element fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.4 Barium solution, stock, 1 mL = 1000 µg Ba: Dissolve 1.5163 g $BaCl_2$ (element fraction Ba = 0.6595), dried at 250°C for 2 hours, weighed accurately to at least four significant figures, in 10 mL water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.5 Beryllium solution, stock, 1 mL = 1000 µg Be: Do not dry. Dissolve 19.6463 g $BeSO_4 \cdot 4H_2O$ (element fraction Be = 0.0509), weighed accurately to at least four significant figures, in water, add 10.0 mL concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.6 Boron solution, stock, 1 mL = 1000 µg B: Do not dry. Dissolve 5.716 g anhydrous H_3BO_3 (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 1-L volumetric flask with reagent water. Transfer immediately after mixing in a clean polytetrafluoroethylene (PTFE) bottle to minimize any leaching of boron from the glass volumetric container. Use of a non-glass volumetric flask is recommended to avoid boron contamination from glassware.

5.3.7 Cadmium solution, stock, 1 mL = 1000 µg Cd: Dissolve 1.1423 g CdO (element fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a

minimum amount of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.8 Calcium solution, stock, 1 mL = 1000 µg Ca: Suspend 2.4969 g $CaCO_3$ (element Ca fraction = 0.4005), dried at 180°C for 1 hour before weighing, weighed accurately to at least four significant figures, in water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.9 Chromium solution, stock, 1 mL = 1000 µg Cr: Dissolve 1.9231 g CrO_3 (element fraction Cr = 0.5200), weighed accurately to at least four significant figures, in water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.10 Cobalt solution, stock, 1 mL = 1000 µg Co: Dissolve 1.00 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.11 Copper solution, stock, 1 mL = 1000 µg Cu: Dissolve 1.2564 g CuO (element fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.12 Iron solution, stock, 1 mL = 1000 µg Fe: Dissolve 1.4298 g Fe_2O_3 (element fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.13 Lead solution, stock, 1 mL = 1000 µg Pb: Dissolve 1.5985 g $Pb(NO_3)_2$ (element fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.14 Lithium solution, stock, 1 mL = 1000 µg Li: Dissolve 5.3248 g lithium carbonate (element fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.15 Magnesium solution, stock, 1 mL = 1000 µg Mg: Dissolve 1.6584 g MgO (element fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.16 Manganese solution, stock, 1 mL = 1000 µg Mn: Dissolve 1.00 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO_3) and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.17 Mercury solution, stock, 1 mL = 1000 µg Hg: Do not dry, highly toxic element. Dissolve 1.354 g $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL concentrated HNO_3 and dilute to volume in 1-L volumetric flask with reagent water.

5.3.18 Molybdenum solution, stock, 1 mL = 1000 µg Mo: Dissolve 1.7325 g $(NH_4)_6Mo_7O_{24}.4H_2O$ (element fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.19 Nickel solution, stock, 1 mL = 1000 µg Ni: Dissolve 1.00 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated HNO_3, cool, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.20 Phosphate solution, stock, 1 mL = 1000 µg P: Dissolve 4.3937 g anhydrous KH_2PO_4 (element fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.21 Potassium solution, stock, 1 mL = 1000 µg K: Dissolve 1.9069 g KCl (element fraction K = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in water, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.22 Selenium solution, stock, 1 mL = 1000 µg Se: Do not dry. Dissolve 1.6332 g H_2SeO_3 (element fraction Se = 0.6123), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.23 Silica solution, stock, 1 mL = 1000 µg SiO_2: Do not dry. Dissolve 2.964 g NH_4SiF_6, weighed accurately to at least four significant figures, in 200 mL (1:20) HCl with heating at 85°C to effect dissolution. Let solution cool and dilute to volume in a 1-L volumetric flask with reagent water.

5.3.24 Silver solution, stock, 1 mL = 1000 µg Ag: Dissolve 1.5748 g $AgNO_3$ (element fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated HNO_3. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.25 Sodium solution, stock, 1 mL = 1000 µg Na: Dissolve 2.5419 g NaCl (element fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.26 Strontium solution, stock, 1 mL = 1000 µg Sr: Dissolve 2.4154 g of strontium nitrate ($Sr(NO_3)_2$) (element fraction Sr = 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated HCl and 700 mL of water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.27 Thallium solution, stock, 1 mL = 1000 µg Tl: Dissolve 1.3034 g $TlNO_3$ (element fraction Tl = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.28 Tin solution, stock, 1 mL = 1000 µg Sn: Dissolve 1.000 g Sn shot, weighed accurately to at least 4 significant figures, in 200 mL (1:1) HCl with heating to effect dissolution. Let solution cool and dilute with (1:1) HCl in a 1-L volumetric flask.

5.3.29 Vanadium solution, stock, 1 mL = 1000 µg V: Dissolve 2.2957 g NH_4VO_3 (element fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.30 Zinc solution, stock, 1 mL = 1000 µg Zn: Dissolve 1.2447 g ZnO (element fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.4 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Some typical calibration standard combinations are listed in Table 3.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

5.5 Two types of blanks are required for the analysis for samples prepared by any method other than 3040. The calibration blank is used in establishing the analytical curve, and the method blank is used to identify possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial and continuing calibration blank determinations (see Sections 7.3 and 7.4).

5.5.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The Initial Calibration Verification (ICV) is prepared by the analyst by combining compatible elements from a standard source different than that of the calibration standard and at concentrations within the linear working range of the instrument (see Section 8.6.1 for use).

5.7 The Continuing Calibration Verification (CCV)) should be prepared in the same acid matrix using the same standards used for calibration at a concentration near the mid-point of the calibration curve (see Section 8.6.1 for use).

5.8 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1 through 3.3.

7.0 PROCEDURE

7.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater samples which have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Solubilization and digestion procedures are presented in Sample Preparation Methods (Chapter Three, Inorganic Analytes).

7.2 Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration). Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer.

7.2.1 Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data document the selection criteria of background correction points; analytical dynamic ranges, the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis. These documented data must be kept on file and be available for review by the data user or auditor.

7.2.2 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions cannot be provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for

a task. Operating conditions for aqueous solutions usually vary from 1100 to 1200 watts forward power, 14 to 18 mm viewing height, 15 to 19 liters/min argon coolant flow, 0.6 to 1.5 L/min argon nebulizer flow, 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. For an axial plasma, the conditions will usually vary from 1100-1500 watts forward power, 15-19 liters/min argon coolant flow, 0.6-1.5 L/min argon nebulizer flow, 1-1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. Reproduction of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively, by adjusting the argon aerosol flow has been recommended as a way to achieve repeatable interference correction factors.

7.2.3 The plasma operating conditions need to be optimized prior to use of the instrument. This routine is not required on a daily basis, but only when first setting up a new instrument or following a change in operating conditions. The following procedure is recommended or follow manufacturer's recommendations. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure.

7.2.3.1 Ignite the radial plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. While aspirating a 1000 ug/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

7.2.3.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate; set the peristaltic pump to deliver the rate in a steady even flow.

7.2.3.3 Profile the instrument to align it optically as it will be used during analysis. The following procedure can be used for both horizontal and vertical optimization in the radial mode, but is written for vertical. Aspirate a solution containing 10 ug/L of several selected elements. These elements can be As, Se, Tl or Pb as the least sensitive of the elements and most needing to be optimize or others representing analytical judgement (V, Cr, Cu, Li and Mn are also used with success). Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the load coil. (This region of the plasma is referred to as the analytical zone.) Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the best net intensity ratios for the elements analyzed or the highest intensity ratio for the least

sensitive element. For optimization in the axial mode, follow the instrument manufacturer's instructions.

7.2.3.4 The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits.

7.2.3.5 If either the instrument operating conditions, such as incident power or nebulizer gas flow rate are changed, or a new torch injector tube with a different orifice internal diameter is installed, the plasma and viewing height should be re-optimized.

7.2.3.6 After completing the initial optimization of operating conditions, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction in particular are discussed in the section on interferences. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls within ± one reporting limit from zero. The upper control limit is the analyte instrument detection limit. Once established the entire routine must be periodically verified every six months. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verification of the routine should be kept on file. Special cases where continual verification is required are described elsewhere.

7.2.3.7 Before daily calibration and after the instrument warmup period, the nebulizer gas flow rate must be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate, In order to maintain valid spectral interelement correction routines the nebulizer gas flow rate should be the same (< 2% change) from day to day.

7.2.4 For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements.

7.2.5 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

7.2.5.1 Method detection limits must be established for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3-5 times the anticipated detection limit. Refer to Chapter One for additional guidance on the performance of MDL studies.

7.2.5.2 Determination of limits using reagent water represent a best case situation and do not represent possible matrix effects of real world samples.

7.2.5.3 If additional confirmation is desired, reanalyze the seven replicate aliquots on two more non consecutive days and again calculate the method detection limit values for each day. An average of the three values for each analyte may provide for a more appropriate estimate. Successful analysis of samples with added analytes or using method of standard additions can give confidence in the method detection limit values determined in reagent water.

7.2.5.4 The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum for three, preferably five, different concentration standards across the range. One of these should be near the upper limit of the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. The upper range limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined analyte concentrations that are above the upper range limit must be diluted and reanalyzed. The analyst should also be aware that if an interelement correction from an analyte above the linear range exists, a second analyte where the interelement correction has been applied may be inaccurately reported. New dynamic ranges should be determined whenever there is a significant change in instrument response. For those analytes that periodically approach the upper limit, the range should be checked every six months. For those analytes that are known interferences, and are present at above the linear range, the analyst should ensure that the interelement correction has not been inaccurately applied.

NOTE: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self absorption effects. These curves may be used if the instrument allows; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.995 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and recalculated every six months. These curves are much more sensitive to changes in operating conditions than the linear lines and should be checked whenever there have been moderate equipment changes.

7.2.6 The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 5.4. Flush the system with the calibration blank (Section 5.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve must consist of a minimum of a blank and a standard.

7.4 For all analytes and determinations, the laboratory must analyze an ICV (Section 5.6), a calibration blank (Section 5.5.1), and a continuing calibration verification (CCV) (Section 5.7) immediately following daily calibration. A calibration blank and either a calibration verification (CCV) or an ICV must be analyzed after every tenth sample and at the end of the sample run. Analysis of

the check standard and calibration verification must verify that the instrument is within ± 10% of calibration with relative standard deviation < 5% from replicate (minimum of two) integrations. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable ICV, CCV or check standard must be reanalyzed. The analysis data of the calibration blank, check standard, and ICV or CCV must be kept on file with the sample analysis data.

7.5 Rinse the system with the calibration blank solution (Section 5.5.1) before the analysis of each sample. The rinse time will be one minute. Each laboratory may establish a reduction in this rinse time through a suitable demonstration.

7.6 Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported with up to three significant figures.

7.7 The MSA should be used if an interference is suspected or a new matrix is encountered. When the method of standard additions is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences, such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by: multiplying the intensity value for the unfortified aliquot by the volume (Liters) and concentration (mg/L or mg/kg) of the standard addition to make the numerator; the difference in intensities for the fortified sample and unfortified sample is multiplied by the volume (Liters) of the sample aliquot for the denominator. The quotient is the sample concentration.

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution.

NOTE: Refer to Method 7000 for a more detailed discussion of the MSA.

7.8 An alternative to using the method of standard additions is the internal standard technique. Add one or more elements not in the samples and verified not to cause an interelement spectral interference to the samples, standards and blanks; yttrium or scandium are often used. The concentration should be sufficient for optimum precision but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences especially in high solids matrices.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. All quality control measures described in Chapter One should be followed.

8.2 Dilute and reanalyze samples that exceed the linear calibration range or use an alternate, less sensitive line for which quality control data is already established.

8.3 Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water carried through the same preparation process as a sample (refer to Chapter One).

8.4 Analyze matrix spiked duplicate samples at a frequency of one per matrix batch. A matrix duplicate sample is a sample brought through the entire sample preparation and analytical process in duplicate.

8.4.1.1 The relative percent difference between spiked matrix duplicate determinations is to be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(|D_1 + D_2|)/2} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (replicate).

(A control limit of ± 20% RPD or within the documented historical acceptance limits for each matrix shall be used for sample values greater than ten times the instrument detection limit.)

8.4.1.2 The spiked sample or spiked duplicate sample recovery is to be within ± 25% of the actual value or within the documented historical acceptance limits for each matrix.

8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Sections 8.5.1 and 8.5.2, will ensure that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 Dilution Test: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

8.5.2 Post Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

<u>CAUTION</u>: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

8.6 Check the instrument standardization by analyzing appropriate QC samples as follows.

8.6.1 Verify calibration with the Continuing Calibration Verification (CCV) Standard immediately following daily calibration, after every ten samples, and at the end of an analytical run. Check calibration with an ICV following the initial calibration (Section 5.6). At the laboratory's discretion, an ICV may be used in lieu of the continuing calibration verifications. If used in this manner, the ICV should be at a concentration near the mid-point of the calibration curve. Use a calibration blank (Section 5.5.1) immediately following daily calibration, after every 10 samples and at the end of the analytical run.

8.6.1.1 The results of the ICV and CCVs are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.1.2 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.1.3 The results of the calibration blank are to agree within three times the IDL. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within ten percent of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.

8.6.2 Verify the interelement and background correction factors at the beginning of each analytical run. Do this by analyzing the interference check sample (Section 5.8). Results should be within ± 20% of the true value.

9.0 METHOD PERFORMANCE

9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.2 Performance data for aqueous solutions and solid samples from a multilaboratory study (9) are provided in Tables 5 and 6.

10.0 REFERENCES

1. Boumans, P.W.J.M. Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectrometry, 2nd Edition. Pergamon Press, Oxford, United Kingdom, 1984.

2. Sampling and Analysis Methods for Hazardous Waste Combustion; U.S. Environmental Protection Agency; Air and Energy Engineering Research Laboratory, Office of Research and Development: Research Triangle Park, NC, 1984; Prepared by Arthur D. Little, Inc.

3. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

4. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

5. Jones, C.L. et al. An Interlaboratory Study of Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010 and Digestion Method 3050. EPA-600/4-87-032, U.S. Environmental Protection Agency, Las Vegas, Nevada, 1987.

TABLE 1
RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Detection Element	Wavelength[a] (nm)	Estimated IDL[b] (μg/L)
Aluminum	308.215	30
Antimony	206.833	21
Arsenic	193.696	35
Barium	455.403	0.87
Beryllium	313.042	0.18
Boron	249.678x2	3.8
Cadmium	226.502	2.3
Calcium	317.933	6.7
Chromium	267.716	4.7
Cobalt	228.616	4.7
Copper	324.754	3.6
Iron	259.940	4.1
Lead	220.353	28
Lithium	670.784	2.8
Magnesium	279.079	20
Manganese	257.610	0.93
Mercury	194.227x2	17
Molybdenum	202.030	5.3
Nickel	231.604x2	10
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	50
Silica (SiO_2)	251.611	17
Silver	328.068	4.7
Sodium	588.995	19
Strontium	407.771	0.28
Thallium	190.864	27
Tin	189.980x2	17
Titanium	334.941	5.0
Vanadium	292.402	5.0
Zinc	213.856x2	1.2

[a]The wavelengths listed (where x2 indicates second order) are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted (e.g., in the case of an interference) if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 3.1). In time, other elements may be added as more information becomes available and as required.

[b]The estimated instrumental detection limits shown are provided as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c]Highly dependent on operating conditions and plasma position.

TABLE 2
POTENTIAL INTERFERENCES
ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM
INTERFERENCE AT THE 100-mg/L LEVEL[c]

Analyte	Wavelength (nm)	Interferant[a,b] Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al - 1000 mg/L	Mg - 1000 mg/L
Ca - 1000 mg/L	Mn - 200 mg/L
Cr - 200 mg/L	Tl - 200 mg/L
Cu - 200 mg/L	V - 200 mg/L
Fe - 1000 mg/L	

[b] The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

[c] Interferences will be affected by background choice and other interferences may be present.

TABLE 3
MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo
IV	Al, Ca, Cr, K, Na, Ni,Li, and Sr
V	Ag (see "NOTE" to Section 5.4), Mg, Sb, and Tl
VI	P

TABLE 4. ICP PRECISION AND ACCURACY DATA[a]

Element	Sample No. 1				Sample No. 2				Sample No. 3			
	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b] (%)	Accuracy[d] (%)	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b]	Accuracy[d] (%)	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b] (%)	Accuracy[d] (%)
Be	750	733	6.2	98	20	20	9.8	100	180	176	5.2	98
Mn	350	345	2.7	99	15	15	6.7	100	100	99	3.3	99
V	750	749	1.8	100	70	69	2.9	99	170	169	1.1	99
As	200	208	7.5	104	22	19	23	86	60	63	17	105
Cr	150	149	3.8	99	10	10	18	100	50	50	3.3	100
Cu	250	235	5.1	94	11	11	40	100	70	67	7.9	96
Fe	600	594	3.0	99	20	19	15	95	180	178	6.0	99
Al	700	696	5.6	99	60	62	33	103	160	161	13	101
Cd	50	48	12	96	2.5	2.9	16	116	14	13	16	93
Co	700	512	10	73	20	20	4.1	100	120	108	21	90
Ni	250	245	5.8	98	30	28	11	93	60	55	14	92
Pb	250	236	16	94	24	30	32	125	80	80	14	100
Zn	200	201	5.6	100	16	19	45	119	80	82	9.4	102
Se[c]	40	32	21.9	80	6	8.5	42	142	10	8.5	8.3	85

[a]Not all elements were analyzed by all laboratories.
[b]RSD = relative standard deviation.
[c]Results for Se are from two laboratories.
[d]Accuracy is expressed as the mean concentration divided by the true concentration times 100.

TABLE 5

ICP-AES PRECISION AND ACCURACY FOR AQUEOUS SOLUTIONS[a]

Element	Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Accuracy[c] (%)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102
Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Mo	3.70	8	6.9	100
Ni	3.70	7	5.7	100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Ag	3.69	6	9.1	100
Na	14.0	8	4.2	95
Tl	15.1	7	8.5	102
V	3.51	8	6.6	95
Zn	3.57	8	8.3	96

[a]these performance values are independent of sample preparation because the labs analyzed portions of the same solutions

[b]N = Number of measurements for mean and relative standard deviation (RSD).

[c]Accuracy is expressed as a percentage of the nominal value for each analyte in acidified, multi-element solutions.

TABLE 6

ICP-AES PRECISION AND BIAS FOR SOLID WASTE DIGESTS[a]

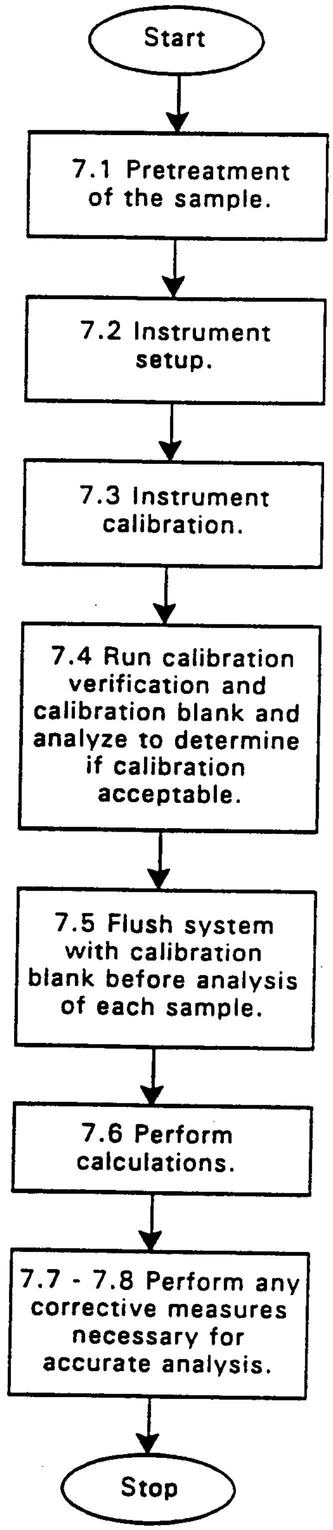
	Spiked Coal Fly Ash (NIST-SRM 1633a)				Spiked Electroplating Sludge			
Element	Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Bias[c] (%AAS)	Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Bias[c] (%AAS)
Al	330	8	16	104	127	8	13	110
Sb	3.4	6	73	96	5.3	7	24	120
As	21	8	83	270	5.2	7	8.6	87
Ba	133	8	8.7	101	1.6	8	20	58
Be	4.0	8	57	460	0.9	7	9.9	110
Cd	0.97	6	5.7	101	2.9	7	9.9	90
Ca	87	6	5.6	208	954	7	7.0	97
Cr	2.1	7	36	106	154	7	7.8	93
Co	1.2	6	21	94	1.0	7	11	85
Cu	1.9	6	9.7	118	156	8	7.8	97
Fe	602	8	8.8	102	603	7	5.6	98
Pb	4.6	7	22	94	25	7	5.6	98
Mg	15	8	15	110	35	8	20	84
Mn	1.8	7	14	104	5.9	7	9.6	95
Mo	891	8	19	105	1.4	7	36	110
Ni	1.6	6	8.1	91	9.5	7	9.6	90
K	46	8	4.2	98	51	8	5.8	82
Se	6.4	5	16	73	8.7	7	13	101
Ag	1.4	3	17	140	0.75	7	19	270
Na	20	8	49	130	1380	8	9.8	95
Tl	6.7	4	22	260	5.0	7	20	180
V	1010	5	7.5	100	1.2	6	11	80
Zn	2.2	6	7.6	93	266	7	2.5	101

[a]These performance values are independent of sample preparation because the labs analyzed portions of the same digests.

[b]N = Number of measurements for mean and relative standard deviation (RSD).

[c]Bias for the ICP-AES data is expressed as a percentage of atomic absorption spectroscopy (AA) data for the same digests.

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY



Appendix C-16
Lab Procedure for Total Metals (Hg): Method 7471A

METHOD 7471A

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical instrument detection limit (IDL) for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

3.3 Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the

absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Non-aqueous samples shall be refrigerated, when possible, and analyzed as soon as possible."

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL reagent water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

> CAUTION: Do this addition under a hood, as Cl_2 could be evolved. Add 55 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.2 g of sample. Add 5 mL of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4. Refer to the caution statement in section 7.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles or equivalent. Add enough reagent water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL reagent water and 15 mL of $KMnO_4$ solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.6 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into

account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

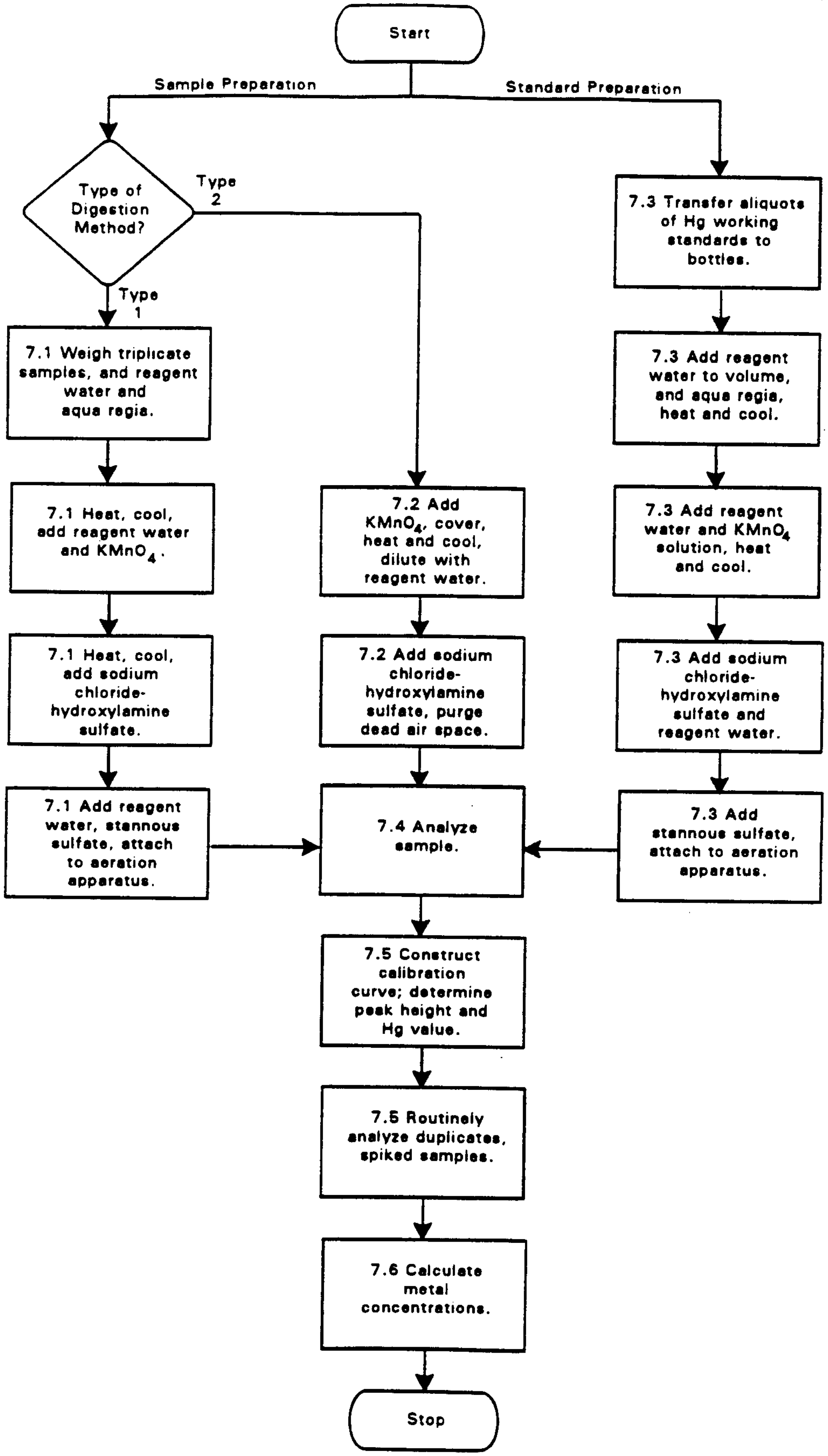
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 ug/g
Wastewater treatment sludge	Not known	0.4, 0.28 ug/g

METHOD 7471A
MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)



Appendix C-17
Lab Procedure for Total Metals (Se): Method 7740

METHOD 7740

SELENIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7740 is an atomic absorption procedure approved for determining the concentration of selenium in wastes, mobility-procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7740, samples must be prepared in order to convert organic forms of selenium to inorganic forms, to minimize organic interferences, and to convert samples to suitable solutions for analysis. The sample-preparation procedure varies, depending on the sample matrix. Aqueous samples are subjected to the acid-digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of lamp radiation during atomization will be proportional to the selenium concentration.

2.3 The typical detection limit for this method is 2 ug/L.

3.0 INTERFERENCES

3.1 Elemental selenium and many of its compounds are volatile; therefore, samples may be subject to losses of selenium during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, selenium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Selenium analysis is particularly susceptible to these problems because of its low analytical wavelength (196.0 nm). Simultaneous background correction is required to avoid erroneously high results. High iron levels can give overcorrection with deuterium background. Zeeman background correction can be useful in this situation.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

3.5 Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). The addition of nickel nitrate such that the final concentration is 1% nickel will lessen this interference.

4.0 APPARATUS AND MATERIALS

4.1 <u>250-mL Griffin beaker</u>.

4.2 <u>10-mL volumetric flasks</u>.

4.3 <u>Atomic absorption spectrophotometer</u>: Single- or dual-channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm, and provisions for simultaneous background correction and interfacing with a strip-chart recorder.

4.4 <u>Selenium hollow cathode lamp, or electrodeless discharge lamp (EDL)</u>: EDLs provide better sensitivity for the analysis of Se.

4.5 <u>Graphite furnace</u>: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 <u>Strip-chart recorder</u>: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis, such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 <u>Pipets</u>: Microliter with disposable tips. Sizes can range from 5 to 1,000 uL, as required.

5.0 REAGENTS

5.1 <u>ASTM Type II water</u> (ASTM D1193): Water should be monitored for impurities.

5.2 <u>Concentrated nitric acid</u> (HNO_3): Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.3. <u>Hydrogen peroxide</u> (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank made with the oxidant is <MDL, the oxidant can be used.

5.4 Selenium standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (actual assay 94.6% H_2SeO_3, analytical reagent grade) or equivalent in Type II water and dilute to 200 mL.

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in Type II water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with Type II water.

5.7 Selenium working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3, 2 mL of 30% H_2O_2, and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with Type II water.

5.8 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.9 Hydrogen: Suitable for instrumental analysis.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Steps 7.1.1 to 7.1.3. Sludge-type samples should be prepared according to Method 3050. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 mL of well-mixed sample to a 250-mL Griffin beaker; add 2 mL of 30% H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool and bring back to 50 mL with Type II water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution, and dilute to 10 mL with Type II water. The sample is now ready for injection into the furnace.

7.2 The 196.0-nm wavelength line and a background correction system must be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured uL-aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.6 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Duplicates, spiked samples, and check standards should be analyzed every 20 samples.

7.8 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 270.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

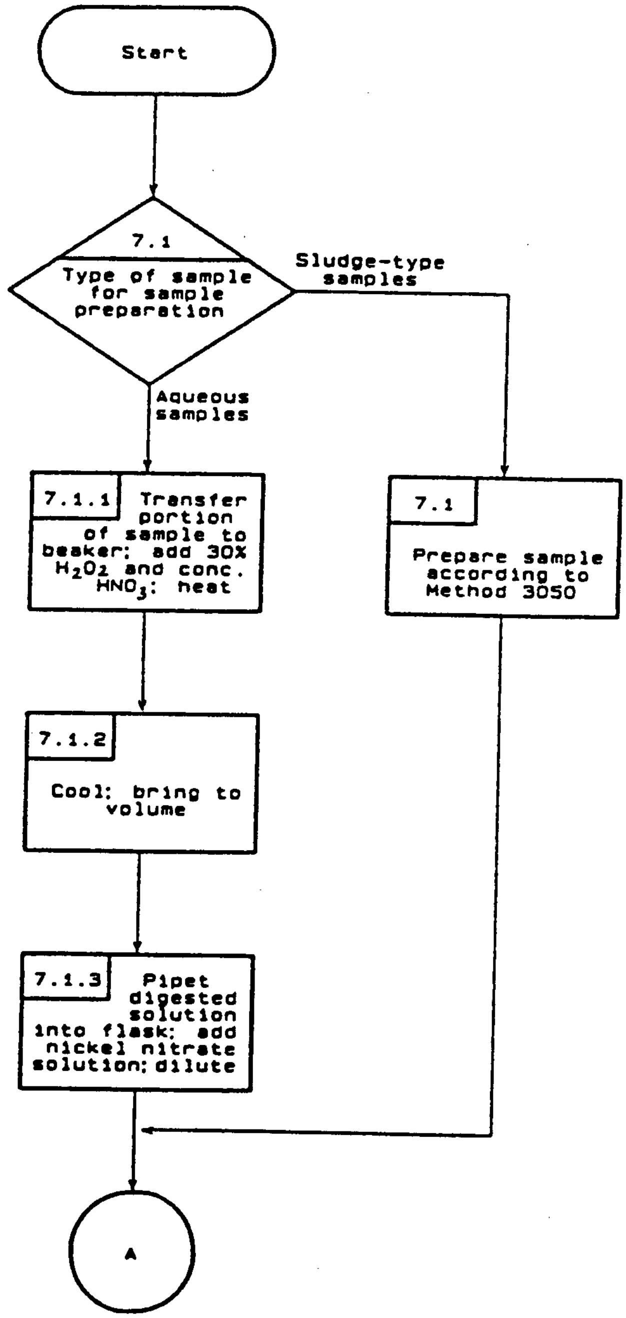
10.0 REFERENCES

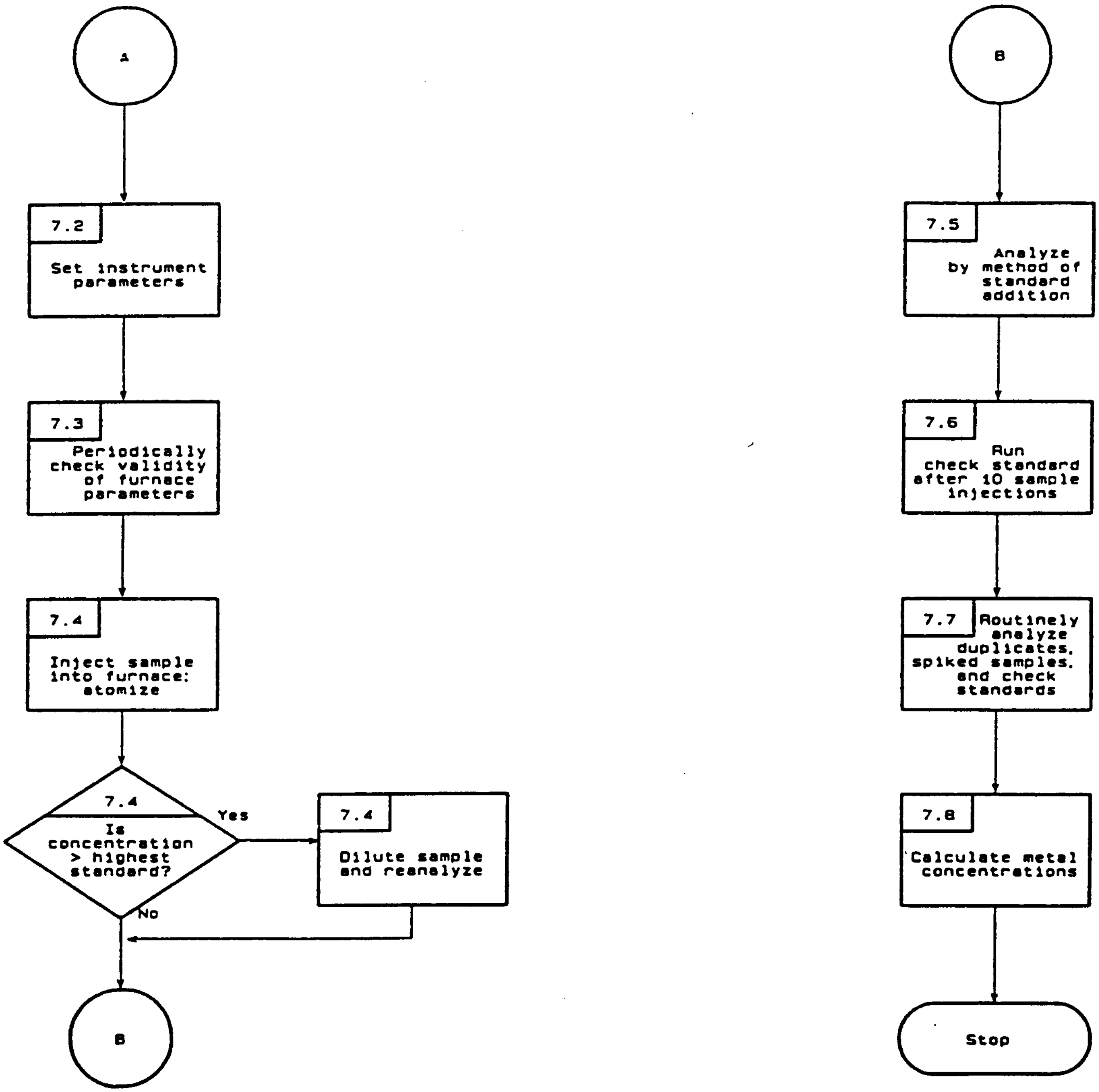
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 270.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	3050	14, 11 ug/g


Start
7.1
Type of sample for sample preparation
Sludge-type samples
Aqueous samples
7.1.1 Transfer portion of sample to beaker; add 30% H_2O_2 and conc. HNO_3; heat
7.1 Prepare sample according to Method 3050
7.1.2 Cool; bring to volume
7.1.3 Pipet digested solution into flask; add nickel nitrate solution; dilute
A


A
7.2
Set instrument parameters
7.3
Periodically check validity of furnace parameters
7.4
Inject sample into furnace: atomize
7.4
Is concentration > highest standard?
Yes
7.4
Dilute sample and reanalyze
No
B
B
7.5
Analyze by method of standard addition
7.6
Run check standard after 10 sample injections
7.7
Routinely analyze duplicates, spiked samples, and check standards
7.8
Calculate metal concentrations
Stop

Appendix C-18
Lab Procedure for Total Metals: Sequential Extraction for Soil

1.0 PURPOSE

This procedure describes an analytical process for partitioning of soil bound particulate trace metals (Cd, Co, Cu, Ni, Pb, Zn, Fe and Mn) into five fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residual.

2.0 SCOPE

This procedure applies to soil samples from studies of phytoremediation of lead contaminated soils.

3.0 SUMMARY

A two gram sample of soil or sediment is subjected to extraction by five different chemical reagents each progressively more reactive to the sample (magnesium chloride, then sodium acetate, then hydroxylamine hydrochloride in acetic acid, then nitric acid and hydrogen peroxide and finally hydrofluoric and perchloric acids). Complementary measurements are then performed on the individual leachates and on the residual solids following each extraction to evaluate the selectivity of the various metals (Cd, Co, Cu, Ni, Pb, Zn, Fe and Mn) toward specific geochemical phases.

4.0 REFERENCES

4.1 "Sequential Extraction for the Speciation of Particulate Trace Metals", Tessier, A., P.G.C. Campbell and M. Bisson. 1979. Anal. Chem. 51:844-850.

4.2 Method 6010A, "Inductively Coupled Plasma - Atomic Emission Spectroscopy", Test Methods for Evaluating Solid Waste, Physical/ Chemical Methods, SW-846, 3rd Edition, Most Recent Update (July 1992 with proposed methods dated November 1992)

4.3 "Standard Specification for Reagent Water", ASTM D1193-91, 1996 Annual Book of ASTM Standards, Volume 11.01, Water and Environmental Technology, p.116-118

5.0 RESPONSIBILITIES

5.1 The laboratory supervisor, or his designee, shall ensure that this procedure is followed during the sequential extraction for the speciation of particulate trace metals.

5.2 The laboratory group leader, or his designee, shall delegate the performance of this procedure to personnel experienced with this procedure and is responsible for the training of new personnel on this procedure. Data shall be reviewed by the laboratory group leader or his designee.

5.3 The analyst shall follow this procedure and report any abnormal results or nonconformance to the laboratory group leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 All sample containers must be prewashed with detergents, acids and ASTM Type II water. Plastic and glass containers are both suitable.

6.1.2 Samples shall be refrigerated upon receipt and analyzed as soon as possible.

6.1.3 All samples shall be air dried at room temperature to a constant weight and ground to pass through a #10 sieve.

6.2 Limitations and Actions

For this procedure, a batch is defined as a group of no more than 20 samples extracted at the same time with the same set of reagents.

6.3 Requirements

.6.3.1 Apparatus/Equipment

6.3.1.1 Analytical balance: capable of weighing to 0.1 mg

6.3.1.2 Centrifuge: capable of centrifuging at 10,000 rpm

6.3.1.3 Centrifuge tubes: polypropylene, 50 ml

6.3.1.4 pH meter with appropriate electrode

6.3.1.5 Platinum crucibles

6.3.1.6 Magnetic stirrer and stirring bars

6.3.1.7 Laboratory oven

6.3.1.8 Normal laboratory glassware

6.3.2 Reagents and Standards

6.3.2.1 ASTM Type II water (ASTM D1193): Water shall be monitored for impurities by conductivity (conductivity of less than 1.0 µmho/cm at 25°C).

6.3.2.2 Magnesium chloride: reagent grade

6.3.2.3 Magnesium chloride, 1M: weigh 95.23 g of reagent grade magnesium chloride into a 1 liter volumetric flask and dilute to volume with ASTM Type II water

6.3.2.4 Glacial acetic acid: reagent grade

6.3.2.5 Sodium acetate: reagent grade

6.3.2.6 Sodium acetate, 1M: weigh 82.04 g of reagent grade sodium acetate into a 1 liter volumetric flask and dilute to volume with ASTM Type II water

6.3.2.7 Carbonate extracting solution: 1 M sodium acetate adjusted to pH 5.0 with glacial acetic acid

6.3.2.8 Hydroxylamine hydrochloride: reagent grade

6.3.2.9 Hydroxylamine hydrochloride, 0.04 M in 24% acetic acid: Weigh 2.780 g of hydroxylamine hydrochloride into a 1 liter flask and dissolve in 500 ml ASTM Type II water. Add 250 ml glacial acetic acid and make to volume with ASTM Type II water.

6.3.2.10 Nitric acid: concentrated, reagent grade

6.3.2.11 Nitric acid, 0.02 M: add 1.27 ml of concentrated, reagent grade nitric acid to 500 ml of ASTM Type II water in a 1 liter flask, swirl to mix and make to volume with ASTM Type II water

6.3.2.12 Hydrogen peroxide, 30%: reagent grade

6.3.2.13 Hydrogen peroxide, 30% adjusted to pH 2: Add concentrated reagent grade nitric acid to 30% reagent grade hydrogen peroxide until the pH drops to 2.0

6.3.2.14 Ammonium acetate: reagent grade

6.3.2.15 Ammonium acetate, 3.2 M in 20% nitric acid: Add 246.66 g of reagent grade ammonium acetate to 500 ml ASTM Type II water in a 1 liter volumetric flask and swirl to dissolve. Add 200 ml concentrated reagent grade nitric acid, swirl and make to volume with ASTM Type II water.

6.3.2.15 Hydrofluoric acid: reagent grade

6.3.2.16 Perchloric acid: concentrated, reagent grade

6.3.2.17 Hydrochloric acid: concentrated, reagent grade

7.0 <u>PROCEDURE</u>

7.1 Procedure Instructions

7.1.1 Weigh a 2 gram sample of dried (room temperature) soil or sediment into a 50 ml polypropylene centrifuge tube.

7.1.2 Add 16 ml of magnesium chloride solution and stir on a magnetic stirrer for 1 hour.

7.1.3 Centrifuge at 10,000 rpm for 30 minutes.

7.1.4 Remove supernatant with a pipette and submit this solution for analysis of trace metals by ICP. This is the exchangeable fraction.

7.1.5 Add 16 ml of ASTM Type II water to the centrifuge tube, suspend the solids by stirring and centrifuge at 10,000 rpm for 30 minutes.

7.1.6 Remove this wash solution with a pipette and discard it.

7.1.7 Add 16 ml of 1 M sodium acetate adjusted to pH 5.0 with acetic acid.

7.1.8 Stir continuously for 5 hours.

7.1.9 Centrifuge at 10,000 rpm for 30 minutes.

7.1.10 Remove the supernatant with a pipette and submit this solution for analysis of trace metals by ICP . This is the fraction bound to carbonates.

7.1.11 Add 16 ml of ASTM Type II water and suspend the solids by stirring.

7.1.12 Centrifuge at 10,000 rpm for 30 minutes.

7.1.13 Remove this wash solution with a pipette and discard it.

7.1.14 Add 40 ml of 0.04 M hydroxylamine hydrochloride in 25% acetic acid and stir to suspend solids.

7.1.15 Place in a laboratory oven set at 96°C and heat with occasional agitation for 6 hours.

7.1.16 Cool and centrifuge at 10,000 rpm for 30 minutes.

7.1.17 Remove the supernatant with a pipette and submit this sample for analysis of trace metals by ICP. This fraction is defined as the fraction bound to Fe-Mn oxides.

7.1.18 Add 16 ml of ASTM Type II water and stir to suspend solids.

7.1.19 Centrifuge at 10,000 rpm for 30 minutes.

7.1.20 Remove the wash solution with a pipette and discard it.

7.1.21 Add 6 ml of 0.02 M HNO_3 and 10 ml of H_2O_2 adjusted to pH 2 with HNO_3 and heat in a laboratory oven at 85°C for 2 hours with occasional agitation.

7.1.22 Add a second aliquot of 10 ml of 30% H_2O_2 (pH 2 with HNO_3) and heat an additional 3 hours in a laboratory oven at 85°C with intermittent agitation.

7.1.23 Cool and add 10 ml of 3.2 M ammonium acetate in 20% HNO_3 and dilute to 40 ml.

7.1.24 Stir continuously for 30 minutes.

7.1.25 Centrifuge at 10.000 rpm for 30 minutes.

7.1.26 Remove the supernatant with a pipette and submit for analysis of trace metals by ICP. This is the fraction bound to organic matter.

7.1.27 Add 16 ml of ASTM Type II water and stir to suspend solids.

7.1.28 Remove wash solution with a pipette and discard it.

7.1.29 Transfer the residue to a platinum crucible.

NOTE: The steps 7.1.30, through 7.1.33 must be performed in a perchloric acid hood.

7.1.30 Add 1 ml $HClO_4$ and 15 ml HF and evaporate to near dryness without boiling.

7.1.31 Add a second aliquot of 1 ml $HClO_4$ and 15 ml HF and again evaporate to near dryness without
boiling.

7.1.32 Add 1 ml $HClO_4$ and heat until the appearance of white fumes.

7.1.33 Cool and add 7 ml ASTM Type II water and 4 ml concentrated reagent grade HCl.

7.1.34 Warm to dissolve solids, transfer to a 50 ml volumetric flask and make to volume with ASTM Type II water.

7.1.35 Submit this solution for analysis of trace metals by ICP. This is the residual fraction.

7.2 Quality Control Sample Requirements

7.2.1 One duplicate sample will be analyzed for every batch.

7.2.2 One method blank will be analyzed for every batch.

7.2.3 A matrix spike will be analyzed for each batch for each of the five sequential extractions. To 10 ml of each extract solution, 1 ml of a 100

mg/L standard will be added. (The spike concentration will then be 9.09 mg/L.)

Note: Smaller quantities may be used in the same ratio if sample size does not permit using 10 ml.

8.0 SAFETY

8.1 Concentrated perchloric acid can react explosively with organic material such as paper or plant tissue. Caution is advised. Work with perchloric acid in a perchloric acid hood which has been specifically designed for operations with that chemical.

8.1 General laboratory safety rules shall be observed.

9.0 NOTES

None

10.0 ATTACHMENTS AND APPENDICES

None

END OF PROCEDURE

Appendix C-19
Lab Report for Total Metals: Scanning Electron Microscope for Plants

To: Paul Pier, CEB 1C-M,Muscle Shoals, Al 35661
David Behel, CTR 1K-M, Muscle Shoals, Al 35661

From: Henry Copeland, CTR 1K-M, Muscle Shoals, Al 35661

Date: May 21, 1998

Subject: **ANALYSIS OF CORN PLANT FOR LEAD**

Background

Samples of a corn plant from column 12 site 7 were analyzed per your request. A sample of the leaf, about 6 inches from the end, was taken. A sample of the stalk on the same plant near the base was also taken.

Two sections of the leaf sample were mounted on a 25 mm mounting stud using carbon conductive tabs. One of the sections was mounted with the top side up. The other was mounted with the top side down.

Two section of the stalk and the associated pulp were mounted on the same stud. One of the stalk sections was mounted with outside up, the other with outside down. The pulp was mounted on the same stud.

On a 13 mm stud with carbon conductive tabs, a section of the leaf sample was mounted with a cross section view up. A section of the stalk was mounted on the same stud with a cross section view up.

Discussion

The samples were analyzed using an ElectroScan environmental scanning electron microscope (ESEM) and a PGT energy dispersive X-ray (EDX) and X-ray imaging system that is integral to the ESEM. The samples were examined in their natural state with no coating applied.

The material on the 25 mm stud were examined. X-ray spectrum obtained and X-ray images were obtained. For the leaf section, both stoma and non-stoma areas were examined using partial field scanning to restrict the spectrum to the selected area. X-ray images were made from the same general area. The stalk and pulp sections were examined and X-ray spectrum were obtained.

The leaf cross section on the 13 mm stud was examined. X-ray spectrum were obtained using spot scan to examine the interior and exterior of the leaf. The inner surface of a vein was also examined using a spot scan. An X-ray images of the section was obtained.

Conclusions

Lead was found in the leaf sections. No measurable lead was found in the stalk and pulp sections.

The lead in the leaf section was distributed throughout the leaf. It did not appear to be associated with any structure in the leaf.

X-ray spectra and images of the analysis have been provided to you. If you need any further information or analysis please contact me at 386-3762.

Appendix C-20
Lab Procedure for Water and EDTA Extractable Lead: Method ASA 21-5

Bio-Available Lead
(Water Extractable Lead)
ASA Method 21-5

1.0 Procedure

Extract 5.0 grams (dry weight) soil with 50 ml water for three hours on a reciprocating shaker at 180 cycles per minute. Centrifuge the sample as needed and then filter the supernatant through a 1-micron syringe filter. Acidify a 10-ml portion of the filtered sample with 10 ml nitric acid and dilute to 50 ml.

Submit for lead analysis by inductively coupled plasma (ICP). Report sample weight, percent moisture, extraction volume and dilution factor to the metals workgroup so that analytical values may be calculated.

2.0 Recordkeeping

Retain all worksheets, calculations, graphs, and notes.

3.0 Quality Control Samples

Duplicate samples may be extracted as quality control samples. Other quality control samples such as matrix spikes may be performed on extracts as required by the metals analytical procedure.

4.0 References

"Selective Extraction," Section 21-5 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

EDTA Extraction of Lead from Soils
ASA 21-5

Reagent:

0.1 M EDTA Solution

Dissolve 37.2 g Ethylenedinitrilo Tetraacetic Acid Disodium Salt, Dihydrate in approximately 800 ml deionized water in a volumetric flask. Bring the volume to one liter with deionized water.

Procedure:

1. Place 10 g dry soil in 125 ml Erlenmeyer flask.
2. Add 20 ml of EDTA extracting solution.
3. Shake for 2 hours on an oscillating shaker on low setting (180/min).
4. Filter extract through previously folded Whatman 42 filter paper into a 50 ml Erlenmeyer beaker.
5. Submit the filtrates for analysis by inductively coupled plasma (ICP) or atomic absorption.

References:

"Selective Extraction," Section 21-5 in *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, Second Edition, A. L. Page Editor, American Society of Agronomy, Inc. 1982

Miller, J. E., J. J. Hassett, and D. E. Koeppe, 1975, Commun. Soil Sci. Plant Analy. 6:339-347

Appendix C-21
Lab Procedure for EDTA Extraction from Soil: Method AP-0057

1.0 PURPOSE

This procedure describes a water extraction method to extract EDTA from soil for subsequent analysis by HPLC.

2.0 SCOPE

Soil samples prepared by this procedure can be analyzed by HPLC.

3.0 SUMMARY

A representative sample not exceeding 30g (wet weight) is stirred vigorously on a magnetic stirrer with an appropriate measured volume of deionized water for two hours. The concentration of EDTA in the liquid portion of the slurry must be less than 200 mg/L to ensure solubility of EDTA complexes. The slurry is then centrifuged and filtered through a 0.2 micron filter. The pH of this solution is then adjusted to 4.5 - 5.0 and then analyzed by HPLC.

4.0 REFERENCES

4.1 ASTM D1193-91, "Standard Specification for Reagent Water," American Society for Testing and Materials.

4.2 AP-0047, "Determination of EDTA by High Performance Liquid Chromatography," Tennessee Valley Authority, Muscle Shoals, Alabama.

5.0 RESPONSIBILITIES

5.1 The Analytical Laboratory Supervisor, or his designee, shall ensure that this procedure is followed during the water extraction of EDTA from soils.

5.2 The Laboratory Group Leader, or his designee, shall delegate the performance of this procedure to personnel experienced with this procedure and is responsible for the training of new personnel on this procedure.

5.3 The analyst shall follow this procedure and report any abnormal results or nonconformance to the Laboratory Group Leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 All sample containers must be prewashed with detergents, acids and ASTM Type II water. Plastic and glass containers are both suitable.

6.1.2 Samples shall be refrigerated upon receipt and analyzed as soon as possible.

6.2 Limitations and Actions

6.2.1 In step 7.2 the EDTA concentration in the aqueous extract must be less than 200 mg/L.

6.3 Requirements

6.3.1 Apparatus/Equipment

6.3.1.1 Erlenmeyer flasks: 50, 125, 250 and 500 ml

6.3.1.2 Watch glasses: 50 and 65 mm

6.3.1.3 Analytical balance: capable of weighing to 0.1 mg

6.3.1.4 Magnetic stirrers and magnetic stirring bars

6.3.1.5 Centrifuge and centrifuge tubes

6.3.1.6 Filter syringes and syringe filters: 0.45 and 0.2 micron nylon syringe filters

6.3.1.7 pH meter and appropriate buffers or short range pH paper (for the range 4.5 - 5)

6.3.2 Reagents and Standards

6.3.2.1 Reagents

6.3.2.1.1 ASTM Type II water (ASTM D1193): Water shall be monitored for impurities by conductivity (conductivity of less than 1.0 umho/cm at 25^0C).

6.3.2.1.2 0.2% Nitric acid: Pipet 0.2 ml reagent grade concentrated nitric acid to a 100 ml volumetric flask and dilute to volume with ASTM Type II water.

6.3.2.2 Standards

None

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity.

7.2 For each sample weigh an appropriate sized sample (not exceeding 30 g wet weight) into an appropriate sized Erlenmeyer flask such that the final concentration of EDTA in the extract is less than 200 mg/L and the resulting slurry fills approximately two-thirds of the volume of the flask.

7.3 Add a measured volume of ASTM Type II water. (From this volume of water plus the water from the moisture analysis of the sample, a total water volume can be calculated.)

7.4 Cover with a watch glass, place sample on a magnetic stirrer and stir vigorously for 2 hours.

7.5 After stirring, pour the slurry (or a portion of the slurry) into a centrifuge tube and centrifuge for 15 minutes at greater than 3000 rpm.

7.6 Using a syringe and syringe filter, filter a portion of the aqueous extract.

7.6 Adjust the pH of the extract to 4.5 - 5.0 with 0.2% nitric acid using a pH meter or short range pH paper.

7.7 Submit for analysis of EDTA by HPLC.

8.0 SAFETY

8.1 General laboratory safety rules shall be observed.

9.0 NOTES

None

10.0 ATTACHMENTS AND APPENDICIES

None

End of Procedure

Appendix C-22
Lab Procedure for EDTA by HPLC: Method AP-0047

1.0 **PURPOSE**

This procedure provides instructions to perform (Ethylene dinitrilo)tetraacetic Acid (EDTA) determinations by high performance liquid chromatography (HPLC). See note 9.1.

2.0 **SCOPE**

This procedure is applicable to aqueous samples or liquid extracts from soil samples.

3.0 **SUMMARY**

Reagent containing ferric ion (Fe^{3+}) is added to all samples and standards. The EDTA forms a complex with the ferric ion to form a UV-absorbing chromophore. The analysis is accomplished using ion-pair HPLC with a diode array detector.

4.0 **REFERENCES**

4.1 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846, 3rd Edition, Most Recent Update (July 1992 with proposed methods dated November 1992)

4.1.1 Chapter 1, "Quality Assurance"

4.1.2 Chapter 4, "Organic Analysis"

4.1.3 Method 8000A, "Gas Chromatography"

4.2 "Extraction of EDTA from Soils", AP-0057, Environmental Applications, Tennessee Valley Authority, Muscle Shoals, Alabama

5.0 **RESPONSIBILITIES**

5.1 The Specialty Laboratory supervisor, or his designee, shall ensure that this procedure is followed during the determination of EDTA.

5.2 The laboratory group leader, or his designee, shall delegate the performance of this procedure to personnel experienced with this procedure. The group leader is responsible for reviewing all data generated. The group leader is responsible for training new personnel on this procedure.

5.3 The chemist or analyst shall follow this procedure, shall ensure the accuracy of all calculations, and shall report any abnormal results or nonconformances to the laboratory group leader.

6.0 REQUIREMENTS

6.1 Prerequisites

6.1.1 All soil samples must be extracted by the method: "Extraction of EDTA from Soils" AP-0057 before analysis.

6.2 Limitations and Actions

6.2.1 High levels of EDTA (>500 ppm) affect the response to EDTA in subsequent samples. Samples following those with high levels of EDTA shall be carefully reviewed and reanalyzed as needed.

6.2.2 All samples reading higher than the calibration curve shall be diluted into the range of the calibration curve.

6.3 Apparatus/Equipment

6.3.1 Analytical balance, capable of reading to 0.1 mg.

6.3.2 HPLC system with diode array detector.

6.3.3 HPLC column, Supelco LC-8DB, 5 micron, 15 cm x 4.6 mm.

6.3.4 Guard column, Supelco LC-ABZ.

6.3.5 Sand bath, constant temperature at approximately 90-95 degrees C.

6.3.6 0.2 micron nylon syringe filter.

6.3.7 0.45 micron, type HA Millipore filter.

6.4 Reagents and Standards

6.4.1 Tetrabutylammonium (dihydrogen) Phosphate (TBAP), reagent grade.

6.4.2 Sodium Hydroxide, NaOH, approximately 25% solution, reagent grade.

6.4.3 Sodium phosphate monobasic, monohydrate, reagent grade.

6.4.4 Phosphoric acid, approximately 40 % solution, reagent grade.

6.4.5 Methanol, HPLC grade.

6.4.6 Ethylenediaminetetraacetic acid, disodium salt, dihydrate (EDTA) reagent grade. Formula weight 372.24 g/mole. Correct all weights of the dihydrate to the anhydrous basis by multiplying by the ratio 336.21/372.24 (0.90321).

6.4.7 Water, HPLC grade.

6.4.8 HPLC Mobile Phase

6.4.8.1 To 400 ml of HPLC grade water, add 1.69g tetrabutylammonium phosphate (TBAP).

6.4.8.2 Add 6.9 g of sodium phosphate monobasic, monohydrate. The pH will be approximately 4.5.

6.4.8.3 Add 100 ml HPLC grade methanol. Mix well.

6.4.8.4 Filter solution through a 0.45 micron type HA millipore filter.

6.4.8.5 Dilute to 1 L with HPLC grade water.

6.4.9 Iron Reagent

6.4.9.1 To 40 ml of HPLC grade water, add 1.69 g of tetrabutylammonium phosphate (TBAP).

6.4.9.2 Add 0.69 g sodium phosphate monobasic, monohydrate.

6.4.9.3 Adjust pH to 3.0 with 0.05 M phosphoric acid.

6.4.9.4 Add 0.5 g ferric nitrate.

6.4.9.5 Mix and allow to stand for 1 hour.

6.4.9.6 Centrifuge solution and decant aqueous phase.

6.4.9.7 Filter the solution through a 0.45 micron type HA millipore filter.

6.4.9.8 Dilute to 100 ml with HPLC grade water.

6.4.10 EDTA, disodium salt, 1000 ppm cal stock. Weigh approximately 0.1 g of EDTA (weighed to the nearest 0.1 mg) and dilute to 100 ml with HPLC grade water. J.T. Baker ultrapure bioreagent.

6.4.11 EDTA, disodium salt, calibration standards. Dilute the 1000 ppm stock standard to produce the following calibration standards: 1 ppm, 5 ppm, 10 ppm, 15 ppm and 20 ppm calibration standards.

6.4.12 EDTA, disodium salt, lab control sample and spiking solution 1000 ppm stock. Weigh approximately 0.1 g of EDTA (weighed to the nearest 0.1 mg) and dilute to 100 ml with HPLC grade water. Reagents, Inc.

6.4.13 EDTA, disodium salt, secondary QC standard. Dilute the 1000 ppm QC stock to produce the following QC standards: 75 ppm spiking solution and 15 ppm QC check standard.

6.5 Quality Control Sample Requirements

6.5.1 Each batch of samples must have the following quality control samples: One spiked sample, one duplicate spike sample, one sample duplicate, one laboratory control sample and one method blank.

6.5.2 The accuracy of the calibration curve is checked on a daily basis with a midpoint check standard analyzed once per every 10 samples analyzed and at the end of the analysis. Recalibration is not required with subsequent analysis unless the midpoint check falls outside the 85 to 115 percent range.

7.0 PROCEDURE

7.1 Calibration

7.1.1 Calibrate the instrument with the following standards: 1 ppm, 5 ppm, 10 ppm, 15 ppm and 20 ppm.

7.1.2 Pipette 1 ml of each known standard into an HPLC sample vial.

7.1.3 Add 0.1 ml of the iron reagent.

7.1.4 Mix thoroughly.

7.1.5 Analyze standards with parameters as in 7.2.3. Utilize vendor-supplied chromatography workstation software to fit the calibration data. Inspect the curve for goodness of fit of 0.99 or better.

7.2 Procedure Instructions

7.2.1 Sample Preparation

7.2.1.1 Filter the aqueous sample through a 0.2 micron nylon syringe filter.

7.2.1.2 Pipette 1 ml of the sample into an HPLC vial.

7.2.1.3 Add 0.1 ml of the iron reagent.

7.2.1.4 Mix thoroughly by shaking.

7.2.3 Instrument Parameters

7.2.3.1 Detector: Photodiode array.

7.2.3.2 Wavelength: 254 nm.

7.2.3.3 Column: Supelcosil LC-8DB; 15 cm x 4.6 mm with guard, LC-ABZ, 2 cm.

7.2.3.4 Flow rate: 1.5 ml/min.

7.2.3.5 Analysis time: 10 minutes.

7.2.3.6 Injection volume: 50 microliters

7.2.4 HPLC Sample Analysis

7.2.4.1 Turn the detector on, allow approximately 1 hour for lamp to warm up.

7.2.4.2 Turn the pump on; 60/40 methanol/water and allow the system to stabilize. NOTE: Prime the pump before operation.

7.2.4.3 Change the composition of the pump to 100% water and allow the system to stabilize.

7.2.4.4 Change the mobile phase of the system to 100% iron reagent mobile phase and allow the system to stabilize.

7.2.4.5 Place the samples on the autosampler and create a sample list. Activate the newly created sample list.

7.2.4.6 Activate the analysis.

7.2.5 Cleaning Column After Analysis

7.2.5.1 Change the mobile phase of the system to 100% water and allow the system to stabilize after the analysis is complete.

7.2.5.2 Change the mobile phase of the system to 60/40 methanol/water and allow the system to stabilize.

7.3 Calculations and Recording Data

7.3.1 The percent recovery for spikes are to be calculated as follows:

$$\% \text{ SPREC} = \frac{\text{SP} - \text{SAMP}}{\text{SP1}} \times 100\%$$

where:

SPREC = Percent spike recovery
SP = Actual spike read
SAMP = Spike's corresponding sample read
SP1 = Theoretical value of spike

7.3.2 The percent recovery for control samples and checks are to be calculated as follows:

$$\% CK = \frac{C1}{C2} \times 100$$

where:

CK = Percent recovery for control sample or check standard.
C1 = Actual known value reading
C2 = Theoretical value of known

7.3.3 Utilize commercial chromatography workstation software or a suitable spreadsheet to apply calibration curve factors to peak heights to calculate concentration in samples

Example: When a calibration curve has been fit to the equation $C = A + Bx$ (where x is observed peak height), the concentration would be calculated as:

Conc = (A + Bx) * Volume / Weight * DF

For a soil sample:

A, B = fit parameters of calibration curve
x = observed peak height
Volume = final extraction volume
Weight = weight of soil extracted, corrected for moisture
DF = dilution factor (when sample was diluted) or 1.000

Reporting units would be mg Disodium EDTA/kg soil

(However, see Note 9.2)

For a liquid sample (direct injection):

A, B = fit parameters of calibration curve
x = observed peak height
Volume = 1.000
Weight = 1.000
DF = dilution factor (when sample was diluted) or 1.000

Reporting units would be mg Disodium EDTA/Liter

7.3.4 File all original data, preparation worksheets, chromatograms, calculations, quality control summary sheets, and printouts with the workorder as quality assurance records.

8.0 SAFETY

8.1 Read Material Safety Data Sheets (MSDS).

8.2 Wear gloves when handling chemicals. Avoid inhalation of dust.

8.3 Wear lab coat and safety glasses while performing this procedure.

8.4 Material Safety Data Sheets (MSDS) are available for tetrabutyl ammonium phosphate, methanol, sodium hydroxide, EDTA, ferric nitrate and sodium phosphate monobasic, monohydrate.

9.0 NOTES

9.1 The chemical names Ethylenediamine tetraacetic acid and (Ethylenedinitrilo)tetraacetic acid are synonyms.

9.2 For the Lead Phytoremediation project, report values as milligrams Disodium EDTA per liter in the extract. Also report sample weight and percent moisture separately.

In this case: Conc = (A + Bx) * Volume / Weight * DF

Where

A, B = fit parameters of calibration curve
x = observed peak height
Volume = final extraction volume
Weight = 1.000
DF = dilution factor (when sample was diluted) or 1.000

10.0 ATTACHMENTS AND APPENDICES

None

End of Procedure

APPENDIX D

SOIL SAMPLING AND EXCAVATION PLANS

Appendix D-1
Soil Sampling Plan for Lead-Contaminated Soil at the Sunflower AAP, Desoto, Kansas

SOIL SAMPLING PLAN

For

LEAD CONTAMINATED SOIL

at the

SUNFLOWER AAP, DESOTO, KANSAS

Prepared for the

U.S. ARMY ENVIRONMENTAL CENTER

Aberdeen Proving Ground, Maryland 21010-5401

and the

U.S. ARMY CORPS OF ENGINEERS

Kansas City District

Prepared by

Tennessee Valley Authority

Environmental Research Center

Muscle Shoals, Alabama 35660-1010

September, 1996

TVA Contract No. RG-99712V

NOTICE

This Soil Sampling Plan for Lead Contaminated Soil at the Sunflower AAP, Desoto, Kansas, was prepared by employees of the Tennessee Valley Authority (TVA) loaned to the U.S. Army Environmental Center (USAEC) at Aberdeen Proving Grounds, Maryland, 21010-5401, pursuant to the provisions of TVA Contract RG-99712V and Military Interdepartmental Purchase Order Request (MIPR) MIPR 9526.

Under that agreement and MIPR, TVA provided the services mutually agreed upon as loaned employees. In regard to the services provided by the TVA employees, sections d and e of the contract and MIPR state as follows:

d. TVA will provide the services of mutually agreed upon loaned employees for purposes of the MIPR. It is expressly understood and agreed that services of such loaned employees will be made available, at TVA's discretion, when the schedule for such services is consistent with TVA's requirements and that TVA does not guarantee the availability of such loaned employees' services at any time during the term of this agreement.

e. It is expressly understood that for all purposes under this MIPR the TVA employees will be acting as loaned employees and will be under the complete supervision and control of the Army at all times and that TVA shall not and cannot supervise or control such employees during the time that they are providing services to the Army. It is further understood and agreed that neither TVA nor any of the loaned employees warrant or guarantee the advice under this agreement and that the Army is solely responsible for determining the suitability and acceptability of such advice and consultations for any purpose. Neither TVA, its agents and employees, nor the loaned employees assume any liability, or responsibility to the Army, its agents, employees, or contractors, or any third party for any costs, charges, damages, (either direct or consequential), demands, claims, or causes of action for any personal injuries (including death) or damage to property, real or personal, or delays arising out of or resulting from any such action or failures to act on the part of such loaned employees whose services are provided under this MIPR.

As provided above, this report was prepared by the TVA loaned employees under direct supervision and control of the U.S. Army. The U.S. Army is solely responsible for its content and use and not TVA, its employees or agents. Wherever it appears in this report, the term "TVA" shall mean TVA loaned employees which are subject to sections d and e quoted.

SECTION 1.0

INTRODUCTION

Disposal and burning of scrap ammunition and powder and similar activities have resulted in contamination of soils by lead (Pb) and other heavy metals at a number of Department of Defense installations. Lead has been identified under CERCLA as a priority element for remediation in contaminated soils, prompting the need for effective procedures for lead removal.

As part of the Department of Defense (DoD) program to evaluate treatment technologies, the U.S. Army Environmental Center (USAEC) has funded a project to assess the effectiveness of phytoremediation procedures for extraction of lead from contaminated soil. In phytoremediation, plants are used to extract lead from the soil and translocate the lead to the plant shoots for removal by harvesting. Soil amendments are used to enhance plant uptake and translocation. This project has been executed under an agreement among the:

- U.S. Army Environmental Center (USAEC)
- Tennessee Valley Authority Environmental (TVAE)

The USAEC and the U.S. Army Corp of Engineers (USACE) Kansas City District are providing contaminated soil from the Sunflower Army Ammunition Plant at Desoto, Kansas. TVAE is providing technical expertise in plant lead uptake, application of soil amendments, and metals analysis for soil and plant samples.

Part of this project consists of screening sources of contaminated soil, collecting samples of this soil, and analyzing the soil to determine the degree of heavy metal contamination. In a later phases of the project, samples of the soil will be excavated and shipped to TVAE's facilities in Muscle Shoals, Alabama , for use in greenhouse experiments.

This sampling plan outlines the methods to be used for collecting lead contaminated soil samples at SFAAP for the purpose of characterizing and mapping selected soil at two sites for soil type and degree and location of lead and other heavy metal contamination. After this procedure is complete TVAE will return to SFAAP for the purpose of excavating the soil to be used in the experiments at Muscle Shoals.

The plan presented here is limited to the soil sampling phase of this project and does not include methods to be used during the soil excavation phase. Sampling procedures for soil excavation will be issued at a later date.

SECTION 2.0

SAMPLING PLAN

2.1 Overview of Sampling Operations

The purpose of the sampling operations will be to characterize and map the soil and the sampling sites for soil type and degree and location of lead and other heavy metal contamination. Sampling will be conducted by collecting multiple soil cores taken at various depths from two contaminated sites.

2.2 Sample Collection and Analytical Procedures

2.2.1 Soil Sampling Procedures (Initial Characterization)

The sampling will be conducted on an explosives burning ground located at the Sunflower Army Ammunition Plant in Desoto, Kansas. The explosives burning ground consists of five approximately 1 acre "cells" plus additional outlying areas of approximately 7-10 acres. Lead contamination in the burning grounds originated from the burning of N-5 propellant, a mixture of organic and Lead-organic compounds. The range of Lead contamination over the burning area is 10-15,800 mg/kg. Other heavy metals are also present in varying concentrations.

Two sites have been selected for soil sampling, one site will be located in Cell 1 and the other in Cell 7 (Figure 2-1). Soil physical analysis shows the soil in Cell 1 to be an alluvial silty clay (50% silt, 50% clay); the soil in Cell 7 is an alluvial silt loam (60% silt, 25% sand, and 15% clay). Cell 7 is within 850 feet of a flowing creek, while Cell 1 is approximately 1500 feet distant. Both cells are located on a sloping, grassy meadow. The soil in this area is classified as alluvial, or that which resulted from water deposition. There is sufficient distance between cells that there is a distinct difference in textural

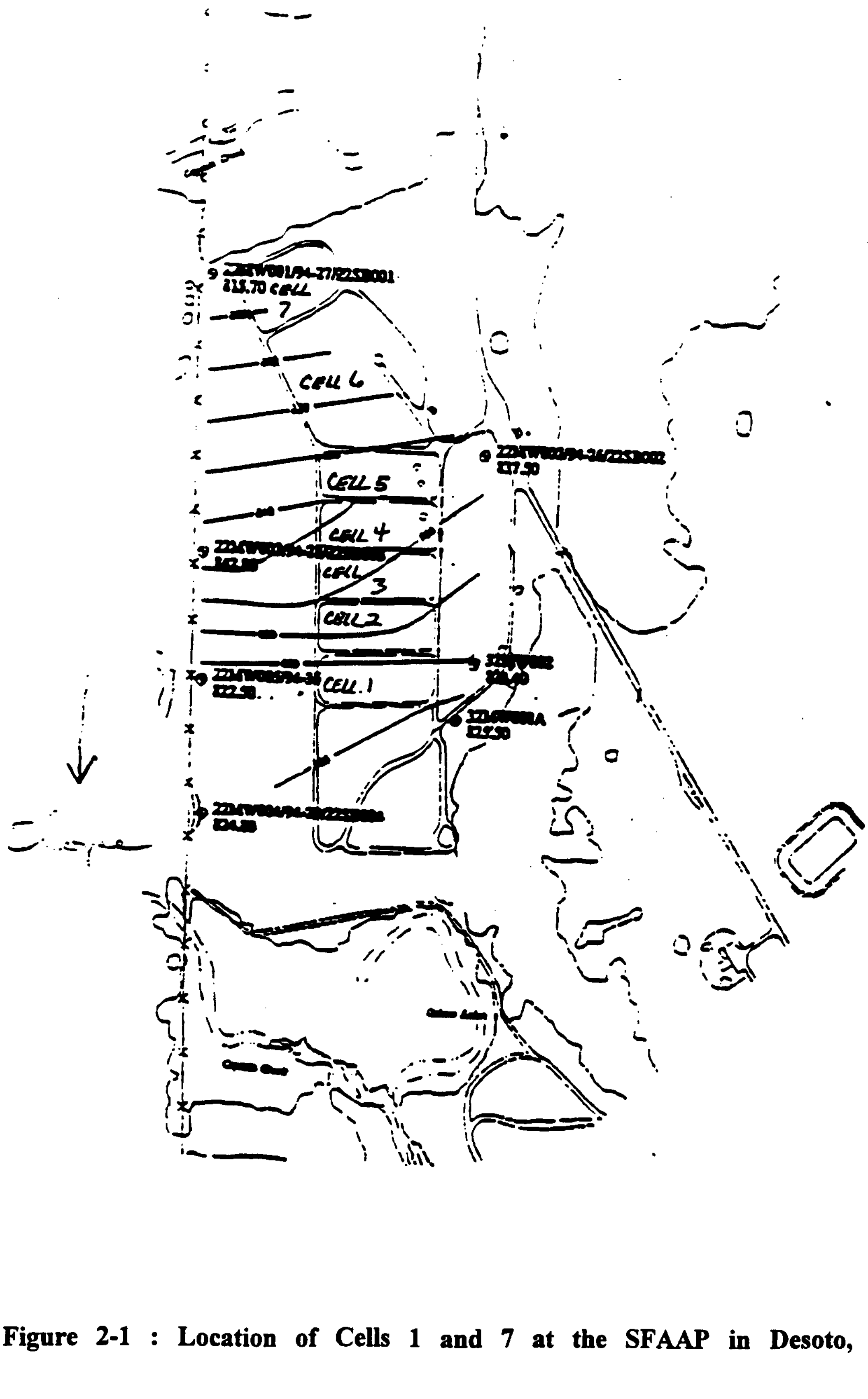


Figure 2-1 : Location of Cells 1 and 7 at the SFAAP in Desoto, Kansas

classification in the soil, and thus for the purpose of this project, the soil may be considered as being of two distinct types.

Soil sampling will be performed by TVA personnel. Safety precautions and site controls to be used during the sampling procedure are outlined in the Health and Safety plan. The sampling procedure will be as follows:

1. TVA personnel will select and mark one 90 feet x 90 feet area within each of Cell 1 and Cell 7.

2. TVA personnel will then subdivide the area into 36 fifteen foot square grids (1 grid every 6 feet).

3. TVA personnel will further subdivide each fifteen foot grid into four seven and one-half foot squares.

4. Then using a hand held soil probe, TVA personnel will take one soil core to a depth of 12 inches from each 7.5 foot square and subdivide this core by depth into two portions (0-6, and 6-12 inches). TVA personnel will then composite the cores taken from the four 7.5 foot squares, according to depth, into one sample for each depth and place into an appropriately identified and labeled plastic zip-loc bags.

5. Package samples for shipment to ERC and transfer to the TVAE's Environmental Applications Analytical Laboratories (EAAL) in Muscle Shoals, AL, in accordance with TVAE's chain of custody procedures (EAAL procedure SP-0001, "Sample Chain of Custody").

A total of 144 samples will be taken (36 grids/site x 2 depths/sample core x 2 sites = 144). Upon leaving the sampling site all TVA personnel involved in the sampling procedure will undergo decontamination as per the Heath and Safety plan.

Appendix D-2
Soil Excavation Plan for Lead-Contaminated Soil at the Sunflower AAP, Desoto, Kansas

DRAFT SOIL EXCAVATION PLAN

For

LEAD CONTAMINATED SOIL

at the

SUNFLOWER AAP, DESOTO, KANSAS

Prepared for the

U.S. ARMY ENVIRONMENTAL CENTER

Aberdeen Proving Ground, Maryland 21010-5401

and the

U.S. ARMY CORPS OF ENGINEERS

Kansas City District

Prepared by

Tennessee Valley Authority

Environmental Research Center

Muscle Shoals, Alabama 35660-1010

October, 1996

TVA Contract No. RG-99712V

NOTICE

This Soil Excavation Plan for Lead Contaminated Soil at the Sunflower AAP, Desoto, Kansas, was prepared by employees of the Tennessee Valley Authority (TVA) loaned to the U.S. Army Environmental Center (USAEC) at Aberdeen Proving Grounds, Maryland, 21010-5401, pursuant to the provisions of TVA Contract RG-99712V and Military Interdepartmental Purchase Order Request (MIPR) MIPR 9526.

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SECTION 1.0

INTRODUCTION

Disposal and burning of scrap ammunition and powder and similar activities have resulted in contamination of soils by lead (Pb) and other heavy metals at a number of Department of Defense installations. Lead has been identified under CERCLA as a priority element for remediation in contaminated soils, prompting the need for effective procedures for lead removal.

As part of the Department of Defense (DoD) program to evaluate treatment technologies, the U.S. Army Environmental Center (USAEC) has funded a project to assess the effectiveness of phytoremediation procedures for extraction of lead from contaminated soil. In phytoremediation, plants are used to extract lead from the soil and translocate the lead to the plant shoots for removal by harvesting. Soil amendments are used to enhance plant uptake and translocation. This project has been executed under an agreement among the:

- U.S. Army Environmental Center (USAEC)
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The USAEC and the U.S. Army Corp of Engineers (USACE) Kansas City District are providing contaminated soil from the Sunflower Army Ammunition Plant at Desoto, Kansas. TVAE is providing technical expertise in plant lead uptake, application of soil amendments, and metals analysis for soil and plant samples.

Part of this project consists of screening sources of contaminated soil, collecting samples of this soil, and analyzing the soil to determine the degree of heavy metal contamination. In a later phases of the project, samples of the soil will be excavated and shipped to TVAE's facilities in Muscle Shoals, Alabama , for use in greenhouse experiments.

This sampling plan outlines the methods to be used for excavating lead contaminated soil at SFAAP for the purpose of using the soil in the experiments at Muscle Shoals. The plan presented here is limited to the soil excavation phase of this project.

SECTION 2.0

SAMPLING PLAN

2.1 Background

During the week of September 23, 1996, TVAE personnel sampled soil at the explosives burning ground located at the Sunflower Army Ammunition Plant in Desoto, Kansas. The explosives burning ground consists of five approximately 1 acre "cells" plus additional outlying areas of approximately 7-10 acres. The soil in the area is generally classified as a Kennebec alluvial silt loam, although there are distinct textural differences ranging from the silt loam to a silty clay. Soil core samples were taken from an area in Cell 1 and from an area in the northern-most outlying area (wherein is located soil drilling site 22MW001/94-27 - see accompanying map, Figure2-1). For the purposes of this plan the northern-most area is designated as Cell 7. Soil physical analysis shows the soil in Cell 1 to be alluvial silty clay; the soil in the Cell 7 is an alluvial silt loam (60% silt, 25% sand, and 15% clay). The Cell 7 is within 850 feet of the northern-most arm of a flowing creek (Captain Creek), while Cell 1 is approximately 1500 feet distant to the south. Both areas are located on a sloping, grassy meadow. There is sufficient distance between cells that there is a distinct difference in textural classification in the soil, and thus for the purpose of this project, the soil may be considered as being of two distinct types.

Lead contamination in the cells originated from the burning of N-5 propellant, a mixture of organic and Pb-organic compounds. The range of Pb contamination over the burning area is 10-15,800 mg/kg. Other heavy metals are also present in varying concentrations

The purpose of the current operation will be to excavate soil from the two sites sampled during TVAE's September visit.

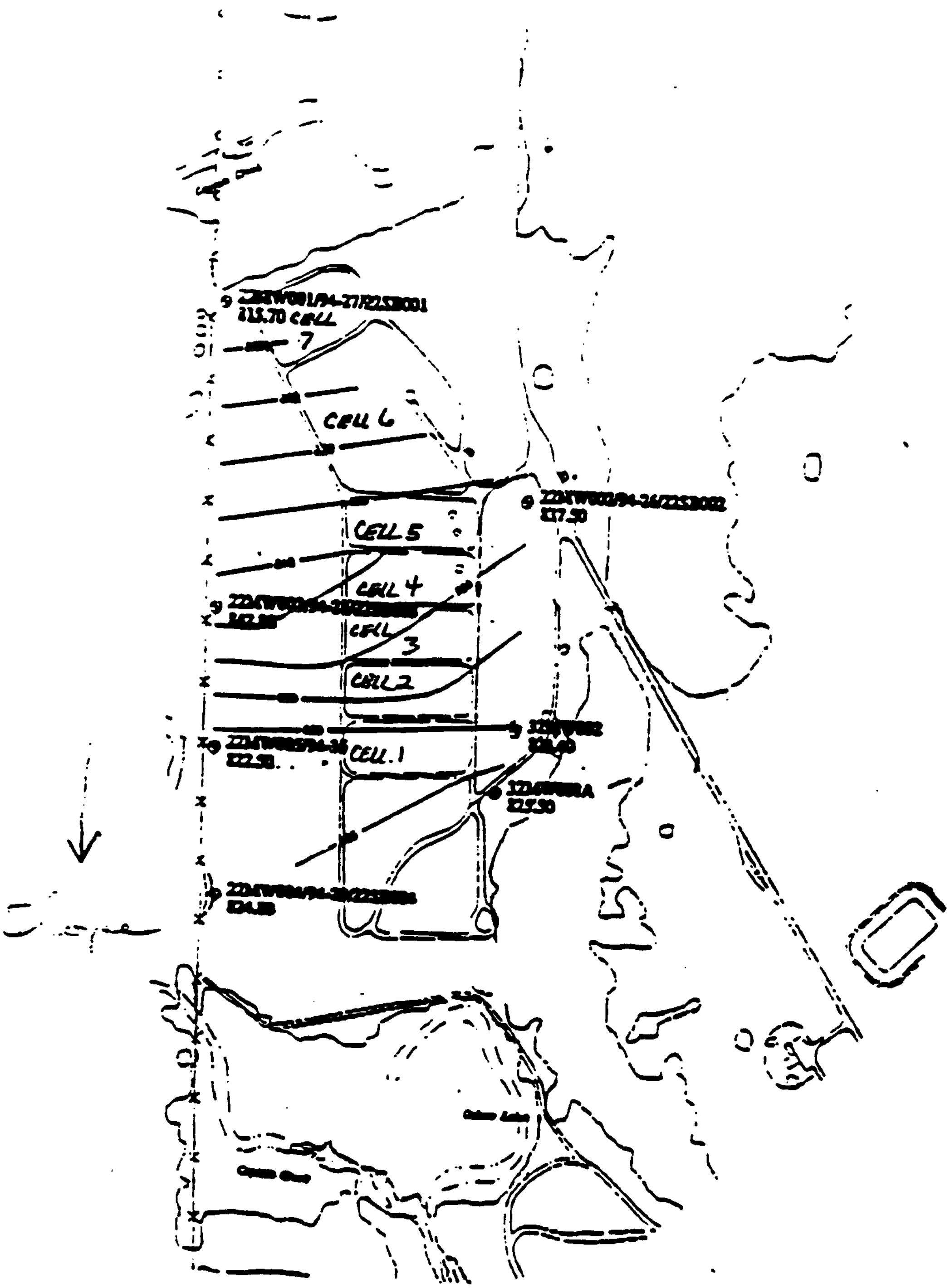

Figure 2-1 : Location of Cells 1 and 7 at the SFAAP in Desoto, Kansas

2.2 Soil Excavation Procedures

During the present operation, soil will be excavated from the two sites sampled during the soil sampling phase of this project. The soil excavation will be performed by TVAE personnel. Safety precautions and site controls to be used during the soil excavation procedure are outlined in the Health and Safety plan. The soil excavation procedure will be as follows:

Based on the criteria of soil texture and total Pb content, bulk quantities of soil will be collected by TVAE personnel from the two sites identified during the sampling phase of this project. 1,000 kg of soil is to be collected from each site. The soil will be collected with hand tools by shoveling the soil into 55 gallon steel drums lined with a heavy duty plastic barrel liner. The soil will be collected to a depth of twelve inches, and there will be a total of about ten drums. The soil in each drum will be labeled appropriately for identification and for DOT regulatory requirements for hazardous waste shipment, and shipped by best available method to ERC, Muscle Shoals, AL.

The procedure will be as follows:

1. Soil will be collected from the previously marked and flagged sampling areas designated in Section 4.2.2.

2. Pre-determine and record the empty weight of the 55 gallon steel drums.

3. Determine the approximate weight of soil excavated by one shovel blade in order to keep a running estimate of the cumulative weight of the soil as it is collected.

4. Collect one shovel full of soil down to 12" depth from each of the four quadrants within each fifteen foot grid and place into plastic-lined 55 gallon steel drums.

5. Load drums onto a suitable vehicle for transport to a weighing station on the Sunflower Plant site and determine the total weight of soil collected by subtracting the pre-recorded weight of each drum from the total weight of soil and drum.

6. Upon leaving the sampling site all TVA personnel involved in the sampling procedure will undergo decontamination as per the Heath and Safety plan.

7. Prepare the appropriate chain of custody documents and ship the containers of soil by motor freight to ERC, Muscle Shoals, AL.

APPENDIX E

SEQUENTIAL METAL ANALYSIS OF SOILS

Table E-1

Soil Leaching Study: Sequential Metal Analysis of Untreated Soil from Cell 1 (Control with Corn)

		Metal Analyses[1]		
Depth (Inches)	**Type of Analyses**	**Lead (mg/kg)**	**Nickel (mg/kg)**	**Zinc (mg/kg)**
0-6	Total	2,570	25.9	108
	Exchangeable	110	0.21	2.16
	Carbonate	633	0.89	7.39
	Fe+Mn Oxide	1,410	11.8	48.7
	Organic	508	2.11	3.85
	Residual	190	10.8	54.9
6-12	Total	2,500	23.9	99.2
	Exchangeable	78.6	1.89	4.35
	Carbonate	633	0.76	8.26
	Fe+Mn Oxide	1,230	7.24	40.1
	Organic	485	3.85	2.77
	Residual	69.2	12.5	64.3
12-18	Total	2,510	24.1	114
	Exchangeable	43.2	1.99	4.15
	Carbonate	627	0.91	9.15
	Fe+Mn Oxide	1,310	10.3	47.5
	Organic	453	4.77	3.78
	Residual	68.9	12.5	70.6
18-30	Total	2,450	23.6	104
	Exchangeable	98.8	2.23	4.99
	Carbonate	484	0.23	6.31
	Fe+Mn Oxide	1,490	13.5	49.7
	Organic	475	3.62	3.67
	Residual	7.16	12.7	60.2

1) Mean of three replicates.

Table E-2

Soil Leaching Study: Sequential Metal Analysis of Soil from Cell 1 Soil Treated with Soil Amendments and Corn

	Metal Analyses[1]			
Depth (Inches)	**Type of Analyses**	**Lead (mg/kg)**	**Nickel (mg/kg)**	**Zinc (mg/kg)**
0-6	Total	2,490	67.3	92.8
	Exchangeable	94.5	0.87	2.56
	Carbonate	534	< 0.2	6.82
	Fe+Mn Oxide	1,400	10.9	49.8
	Organic	481	3.59	3.99
	Residual	6.07	11.65	59.8
6-12	Total	2,400	22.2	98.6
	Exchangeable	76.4	0.61	2.24
	Carbonate	572	1.19	8.25
	Fe+Mn Oxide	1430	14.2	50.9
	Organic	496	3.41	4.39
	Residual	14.8	11.7	58.9
12-18	Total	2,560	22.0	103
	Exchangeable	73.0	0.975	1.88
	Carbonate	565	1.32	7.92
	Fe+Mn Oxide	1,460	12.1	49.4
	Organic	480	3.500	4.2
	Residual	13.9	12.8	61.4
18-30	Total	2,580	23.4	97.1
	Exchangeable	64	0.855	2.14
	Carbonate	642	1.45	8.42
	Fe+Mn Oxide	1,340	1,300	47.8
	Organic	477	3.19	3.79
	Residual	1.44	11.8	59.9

1) Mean of three replicates.

Table E-3

Soil Leaching Study: Sequential Metal Analysis of Untreated Soil from Cell 7

(Control with Corn)

	Metal Analyses[1]			
Depth (Inches)	**Type of Analyses**	**Lead (mg/kg)**	**Nickel (mg/kg)**	**Zinc (mg/kg)**
0-6	Total	3,510	31.7	248
	Exchangeable	166	0.27	7.07
	Carbonate	873	0.6	22.5
	Fe+Mn Oxide	2,110	14.5	149
	Organic	592	4.65	11.4
	Residual	54.7	12.7	69.6
6-12	Total	3,620	31.9	262
	Exchangeable	195	0.38	8.15
	Carbonate	1,070	0.69	26.6
	Fe+Mn Oxide	2,090	14.8	143
	Organic	999	5.62	12.6
	Residual	321	12.9	71.4
12-18	Total	3,660	35.2	252
	Exchangeable	222	< 0.2	8.95
	Carbonate	1,060	0.99	27
	Fe+Mn Oxide	2,100	17.8	147
	Organic	525	3.42	11.7
	Residual	98.2	13.6	74.8
18-30	Total	3,400	29.1	241
	Exchangeable	197	31.0	7.62
	Carbonate	998	1.10	24.8
	Fe+Mn Oxide	2,340	16.2	137
	Organic	672	3.9	9.6
	Residual	104	10.4	69.9

1) Mean of three replicates.

Table E-4

Soil Leaching Study: Sequential Metal Analysis of Cell 7 Soil

Treated with Soil Amendments and Corn

	Metal Analyses[1]			
Depth (Inches)	**Type of Analyses**	**Lead (mg/kg)**	**Nickel (mg/kg)**	**Zinc (mg/kg)**
0-6	Total	3,410	32.6	266
	Exchangeable	209	1.440	9.88
	Carbonate	1,080	0.795	27.3
	Fe+Mn Oxide	2,380	18.4	166
	Organic	794	6.68	16.2
	Residual	188	15.0	81.2
6-12	Total	3,300	31.6	254
	Exchangeable	232	1.740	11.5
	Carbonate	1,020	0.76	26.1
	Fe+Mn Oxide	2,340	19	171
	Organic	723	7.320	15.8
	Residual	128	15.2	78.3
12-18	Total	3,580	30.6	252
	Exchangeable	218	1.16	9.40
	Carbonate	970	0.75	23.7
	Fe+Mn Oxide	2,280	17.0	157
	Organic	840	7.04	15.8
	Residual	225	14.6	82
18-30	Total	3,530	34.5	254
	Exchangeable	212	0.445	9.3
	Carbonate	948	0.72	24.8
	Fe+Mn Oxide	2,230	17.8	160
	Organic	825	7.14	17.0
	Residual	216	14.8	81.6

1) Mean of three replicates.

Table E-5

Soil Leaching Study: Sequential Metal Analysis of Untreated Soil from Cell 1

(Control with White Mustard)

	Metal Analyses[1]			
Depth (Inches)	**Type of Analyses**	**Lead (mg/kg)**	**Nickel (mg/kg)**	**Zinc (mg/kg)**
0-6	Total	2,450	20.8	96
	Exchangeable	127	< 0.2	2.66
	Carbonate	661	1.01	8.55
	Fe+Mn Oxide	1,330	11.1	50.4
	Organic	444	1.97	4.97
	Residual	< 0.75	9.4	53.0
6-12	Total	2,440	21.6	102
	Exchangeable	145	< 0.2	2.61
	Carbonate	651	0.61	7.19
	Fe+Mn Oxide	1,570	13.2	52.7
	Organic	571	4.08	14.6
	Residual	< 0.70	9.34	53.8
12-18	Total	2,400	23.4	97.7
	Exchangeable	151	0.35	3.25
	Carbonate	563	0.85	6.77
	Fe+Mn Oxide	1,370	14.4	46.8
	Organic	469	4.93	4.17
	Residual	< 0.71	11.1	57.0
18-30	Total	2,370	23	102
	Exchangeable	127	< 0.2	2.94
	Carbonate	481	0.77	6.15
	Fe+Mn Oxide	1280	10.5	61.2
	Organic	429	4.2	3.61
	Residual	< 0.69	11.8	58.1

1) Mean of three replicates.

Table E-6

Soil Leaching Study: Sequential Metal Analysis of Cell 1 Soil Treated with Soil Amendments and White Mustard

	Metal Analyses[1]			
Depth (Inches)	**Type of Analyses**	**Lead (mg/kg)**	**Nickel (mg/kg)**	**Zinc (mg/kg)**
0-6	Total	2,330	22.8	103
	Exchangeable	116	1.1	4.09
	Carbonate	642	1.99	8.21
	Fe+Mn Oxide	1,430	12.5	55.3
	Organic	443	1.37	6.15
	Residual	1.20	11.6	52
6-12	Total	2,400	24.4	101
	Exchangeable	137	2.0	3.42
	Carbonate	646	1.72	8.97
	Fe+Mn Oxide	1,490	15.0	49.7
	Organic	555	4.11	49.9
	Residual	1.8	11.4	63.0
12-18	Total	2,510	22.6	107
	Exchangeable	129	1.05	8.07
	Carbonate	470	2.32	7.23
	Fe+Mn Oxide	1,290	14.9	51.9
	Organic	407	5.62	2.98
	Residual	21.1	9.5	59
18-30	Total	2,350	23	107
	Exchangeable	112	2.3	3.24
	Carbonate	464	3.77	8.98
	Fe+Mn Oxide	1,100	13.5	66.9
	Organic	400	2.3	5.12
	Residual	1.99	10.1	78.2

1) Mean of three replicates.

Table E-7

Soil Leaching Study: Sequential Metal Analysis of Untreated Soil from Cell 7 (Control with White Mustard)

		Metal Analyses[1]		
Depth (Inches)	**Type of Analyses**	**Lead (mg/kg)**	**Nickel (mg/kg)**	**Zinc (mg/kg)**
0-6	Total	3,400	32	248
	Exchangeable	222	0.65	8.49
	Carbonate	1,030	0.58	24.2
	Fe+Mn Oxide	2,230	14.9	167
	Organic	604	6.03	11.8
	Residual	120	14.2	119
6-12	Total	3,740	32	245
	Exchangeable	202	< 0.2	7.84
	Carbonate	1,080	1.2	23.7
	Fe+Mn Oxide	2,320	16.6	149
	Organic	958	6.72	13.5
	Residual	238	14.5	71.6
12-18	Total	3,720	31.1	248
	Exchangeable	256	0.66	11.2
	Carbonate	1,250	1.28	27.6
	Fe+Mn Oxide	2,310	16.3	146
	Organic	1,030	6.24	14.1
	Residual	291	13.2	76.1
18-30	Total	3,190	36.3	262
	Exchangeable	233	0.62	9.7
	Carbonate	932	0.84	23.5
	Fe+Mn Oxide	1,840	15.4	128
	Organic	780	5.95	15.1
	Residual	180	13.4	74.2

1) Mean of three replicates.

Table E-8

Soil Leaching Study: Sequential Metal Analysis of Cell 7 Soil Treated with Soil Amendments and White Mustard

	Metal Analyses[1]			
Depth (Inches)	**Type of Analyses**	**Lead (mg/kg)**	**Nickel (mg/kg)**	**Zinc (mg/kg)**
0-6	Total	3,360	27	247
	Exchangeable	203	1.69	10.9
	Carbonate	999	2.08	23.7
	Fe+Mn Oxide	2,150	14.1	171
	Organic	634	5.83	13.1
	Residual	121	16.7	179
6-12	Total	3,540	31	248
	Exchangeable	211	1.7	10.4
	Carbonate	1,000	1.5	25.3
	Fe+Mn Oxide	2,280	17.1	151
	Organic	941	4.70	15.3
	Residual	229	13.9	77.9
12-18	Total	3,300	30.6	258
	Exchangeable	246	2.74	10.4
	Carbonate	1,210	3.19	25.5
	Fe+Mn Oxide	2,200	16.0	149
	Organic	991	8.01	15.9
	Residual	275	10.0	79.4
18-30	Total	3,600	33.1	231
	Exchangeable	234	4.05	12.8
	Carbonate	901	3.11	27.2
	Fe+Mn Oxide	1,840	15.3	107
	Organic	762	7.02	15.0
	Residual	108	14.9	76.3

1) Mean of three replicates.

APPENDIX F

SITE CHARACTERIZATION DATA FOR CELLS 1 AND 7

Table F-1

Total Lead and Soil pH Data Used for Initial Characterization of Site 1

Site 1 Grid No.	Total Lead, mg/kg		Soil pH	
	0"-6"	6"-12"	0"-6"	6"-12"
1	1,490	815	6.9	7.0
2	1,230	634	7.0	6.9
3	292	217	6.8	6.6
4	1,200	396	7.1	7.0
5	553	418	6.8	6.9
6	980	379	6.9	6.8
7	248	55	6.6	6.3
8	101	64	6.0	6.4
9	214	130	6.5	6.3
10	291	58	6.7	6.5
11	206	85	6.5	6.4
12	103	39	6.5	6.2
13	171	43	6.4	6.4
14	64	26	6.3	6.4
15	112	43	6.3	6.4
16	119	506	6.4	6.4
17	62	35	6.3	6.3
18	117	53	6.4	6.4
19	151	38	6.5	6.5
20	111	45	6.4	6.6
21	130	40	6.4	6.5
22	280	197	6.6	6.6
23	210	111	6.4	6.5
24	91	23	6.2	6.4
25	129	36	6.4	6.7
26	73	36	6.5	6.7
27	34	68	6.4	6.3
28	118	39	6.4	6.3
29	188	58	6.9	7.1
30	150	77	7.0	6.9
31	291	72	7.4	7.0
32	312	122	7.0	7.2
33	209	76	6.9	7.1
34	191	88	7.1	6.9
35	397	116	6.9	7.3
36	391	136	7.1	6.8
mean	355	188	6.6	6.7
standard deviation	300	148	1.5	2.4

Table F-2

Total Lead and Soil pH Data Used for Initial Characterization of Site 7

Site 1 Grid No.	Total Lead, mg/kg		Soil pH	
	0"-6"	6"-12"	0"-6"	6"-12"
1	1,460	583	7.3	7.5
2	2,070	1,090	7.3	7.4
3	2,970	2,910	7.3	7.3
4	2,580	886	7.3	7.2
5	3,360	1,740	7.3	7.4
6	4,690	2,630	7.4	7.3
7	1,930	807	7.4	7.4
8	990	452	7.3	7.3
9	707	502	7.1	7.1
10	902	387	7.2	7.1
11	961	605	7.2	7.2
12	1,180	689	7.2	7.1
13	742	1,270	7.0	6.9
14	878	356	7.2	7.1
15	1,090	660	7.0	7.2
16	2,030	1,660	7.1	7.2
17	1,170	1,450	7.0	7.1
18	1,440	400	7.0	7.0
19	519	205	6.8	7.1
20	704	481	6.9	7.2
21	1,190	1,120	7.1	7.3
22	1,730	916	7.2	7.2
23	776	835	7.0	7.0
24	1,270	1,730	7.0	7.0
25	1,360	362	6.9	7.0
26	1,130	1,510	6.9	7.0
27	1,250	895	7.0	7.1
28	2,580	1,670	7.2	7.2
29	3,100	2,600	7.2	7.2
30	2,650	1,560	6.9	7.2
31	1,100	901	6.8	6.9
32	1,010	2,060	7.0	6.9
33	1,800	1,440	7.1	7.0
34	3,100	1,430	7.4	7.3
35	4,230	2,010	7.3	7.3
36	2,410	3,140	7.3	7.4
mean	1,752	1,195	7.1	7.2
standard deviation	1,032	789	0.2	0.2